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Evaluation of Reforming as a Practical Technique for the Elimination of Water Pollution from Wood Gasifiers

by

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March 1984

TEARSHEET ANNOTATION

Reforming was proven, both theoretically and experimentally, to be an effective, cost competitive treatment technology for gasifier condensates.

ABSTRACT

As a first step in the evaluation of the viability of reforming as a technique for the elimination of pollution from gasifier condensate, many of the major constituents were identified from literature sources. A theoretical evaluation of equilibrium constants for the reaction indicated that reformation could be an effective solution. Next an experimental evaluation confirmed that the technique could reduce the contaminants to low levels under relatively mild conditions with catalysts ranging from limestone to typical industrial reforming agents. The reaction appears to be diffusion limited and, as a result, low cost materials, such as limestone, are as effective as conventional nickel catalysts. The reaction rate can be expressed as

$$K = .00197/A \cdot e^{.0033T}$$

where A, a constant between 0.2 and 1, is related to the bulk physical properties of the material.

When extrapolated, these data indicate that the process can be applied to different kinds of gasifiers over a broad size range to reduce pollution levels to acceptable values. Two applications involving a fixed bed and a fluidized bed are discussed.

A very preliminary evaluation indicates that reforming is as effective, if not more so, than other developing technologies. Because of the simplicity of the technology, it is anticipated that it will remain competitive with other technologies as these systems become developed.

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1.0 INTRODUCTION

The increasing emphasis on biomass as a significant long term solution to world-wide energy demands has necessitated a greater need to review the environmental effects of sustained operation of biomass energy conversion facilities. Thermochemical techniques are particularly efficient at converting different forms of biomass into a wide variety of products. Consequently these processes are likely to remain the foundation for biomass use for the foreseeable future. With the ability to provide solid, liquid and gaseous fuels, gasification is perhaps the most flexible of the thermochemical technologies and, although the large scale commercial use of gasification is relatively recent, it is quickly becoming increasingly more widely accepted. Therefore, now is the most propitious time to examine this technology for potential deleterious effects and to develop solutions to alleviate any perceived problems .

Gasification is the thermal restructuring of solid carbonaceous materials into a gaseous energy form. As in many industrial processes, the conversion is not totally complete. For instance, ash and some unreacted carbon are produced as by-products together with a quantity of condensible materials. The ash/carbon residue is relatively inert and its safe disposal by conventional means presents few problems. The condensate, however, contains a

broad diversity of compounds including phenols, polynuclear aromatics and heterocyclic materials. This mixture is not readily biodegradable and contains toxic and potentially mutagenic components. While the condensate problems appear to disfavour the widespread use of gasification, there are two mitigating factors which influence the situation; certain of the gasification technologies produce minimal quantities of organic condensate and, in many applications, these materials are directly consumed during subsequent processing (e.g. by combustion).

The uses for gasification, therefore, play an important role in dictating the need for condensate treatment technology. The objective of gasification is to utilize an alternate energy source, namely biomass, and to substitute for existing fossil fuels when these become depleted or expensive. At present, the principal uses for petroleum fuels and hence the potential applications for biomass involve:

- Combustion for steam raising and process heat
- Direct cycle power generation through reciprocating engines or gas turbines
- Motive force development for transportation
- The production of a broad range of petrochemicals.

In situations in which gasification of biomass supplants

conventional energy use and which involve direct combustion of the hot gas, the organic components in the gas stream are oxidized to carbon dioxide and water and, after particulate removal, the cleaned flue gas can be safely discharged directly to atmosphere. However, there are some applications in which the gas is cooled before it is used e.g. chemical synthesis, reciprocating engine combustion, long distance pipeline transmission and situations which require highly efficient gas cleaning without the use of novel high temperature filtration technology. In each of these circumstances, condensate is produced and the problem of providing an environmentally acceptable disposal solution arises.

Gasification technology, per se, can inherently assist in ameliorating the problem. For instance, units which develop a high temperature zone through which the gasifier products pass, such as downdraft, fluidized bed or entrained bed reactors, tend to induce tar decomposition and generally minimise the production of organic condensates. The origin of this facility is based on the fact that most of these materials are unstable at high temperature and thermally crack or steam reform under the conditions existing in the high temperature zone of the gasifier. This chemistry provides the basis for one of the potential treatment processes for disposal of the organic fraction of the condensate and is the subject of the present report.

2.0 BACKGROUND

Biomass is comprised of polymeric materials principally constituted from carbon, hydrogen and oxygen with minor amounts of chlorine, nitrogen and sulphur. In addition, there is a non-combustible fraction, ash, present in amounts ranging from less than 1% in wood to values as high as 15% for some agricultural residues. In general, the chemical components present in biomass include lignin, cellulose, hemicelluloses and various resins, starches and terpenes.

Cellulose, which is the major component of biomass (about 50%), is a polymeric ring derivative of d-glucose (a C_6 sugar) while the principal hemicelluloses are formed from d-xylose,(a C_5 sugar)and d-mannose,(a C_6 sugar). Lignin on the other hand, is a complex macromolecule primarily based on the phenyl propane unit. It is most probable that each of these materials decompose by different routes during thermal processing and therefore contribute to the diversity of products obtained.

2.1 Gasification Reactions

It is readily apparent that heating of the constituent biomass materials, as occurs in gasification, is a relatively complex process which is dependent both on the heating rate and the final temperature attained. Detailed

reaction mechanisms have been presented by a number of workers; Broido (1976), Shafizadeh et al (1979), Bradbury et al (1979), Baker (1975) and Klein et al (1981). However for the purposes of the present evaluation, it is preferable to use a simplified reaction scheme rather than a detailed hypothesis of typical reaction mechanisms. Thus the following model of the gasification process will be utilized.

The reactions occurring in a typical gasifier can be represented by three simplistic equations involving pyrolysis, gasification and thermal restructuring:

2.1.1 Pyrolysis

After the physically adsorbed water is driven off, the continued heating of biomass yields three phases:

$$\underset{\text{biomass}}{C_aH_bO_c} \longrightarrow \underset{\text{char}}{C_dH_eO_f} + \underset{\text{condensible organic}}{C_mH_nO_o} + \underset{\text{permanent gases}}{C_xH_yO_z} \qquad .....(1)$$

The char comprises about 15 - 30% of the original weight of the feedstock. Also produced is a similar amount of condensible organic material which, in addition to water, contains a wide variety of acyclic and ring compounds with a

broad range of molecular weights. The remaining gaseous phase consists of carbon oxides, hydrogen and the simpler hydrocarbons, primarily methane and ethylene.

The pyrolysis reaction, depending upon operating conditions, can be endo-thermic or exo-thermic.

2.1.2 Gasification

Much of the char produced by pyrolysis is subsequently converted to gas through a series of gasification reactions, the principal of which is with oxygen. It is the exothermicity of this reaction which provides the heat necessary to drive the overall process

$$C_dH_eO_f + xO_2 \rightarrow gCO + (d-g)CO_2 + e/2\ H_2O \quad \text{.....(2)}$$

where $x = d + e/4 - (g+f)/2$

However, there are other reactions which become increasingly important as the char temperature rises above 800°C. These include:

$$C_dH_eO_f + (2d+f-e/2)H_2 \rightarrow dCH_4 + fH_2O \quad \text{.....(3)}$$

$$C_dH_eO_f + (d-f)H_2O \rightarrow dCO + (d+e/2-f)H_2 \quad \text{.....(4)}$$

$$C_dH_eO_f + (d-f+e/2)CO_2 \rightarrow (2d-f+e/2)CO + e/2H_2O \quad \text{...(5)}$$

2.1.3 Thermal Dissociation and Rearrangement

As the volatile components leave the main pyrolysis zone, they continue to rearrange, dissociate and react. Many of the reactions are complex but they can be represented as follows:

$$C_mH_nO_o \rightarrow CO + CO_2 + H_2 + H_2O + C_pH_q + C_rH_sO_t \quad \text{.....(6)}$$

DISSOCIATION/CRACKING

$$C_mH_nO_o + (m-o)H_2O \rightarrow (m-o+n/2)H_2 + mCO \quad \text{.....(7)}$$

REFORMING

Other reactions occurring in the gasifier include:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \text{.....(8)}$$

WATER GAS SHIFT

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad \text{.....(9)}$$

METHANATION

There is, thus, a broad range of chemical compounds produced during the gasification process and many of these appear in the condensed phase.

2.2 Composition of Condensed Phase

Of particular interest to the present study are the quantities and composition of the condensed phase. As described above, the products are quite diverse. However, with the advent of the GC-MS as an analytical technique, it has become easier to identify many of the components present in gasifier condensates. A number of workers, Gurnik et al (1980), Duncan (1981), Inco (1980) and Babu (1981), have identified some of the chemicals found in liquors from different types of gasifiers. The major components described in the literature are summarized in table 1.

The principal component of the condensate liquor is water which is present in the biomass feedstock but is also formed during the pyrolysis and combustion reactions. Typically the water content of the gasifier product stream lies in the range of 5 to 30 mol %. However, the yield of the condensible organic components covers a much broader spectrum i.e. 0.1 to 6 wt. % of the raw biomass - the specific quantities being directly related to the nature of the gasifier design. For instance, downdraft and fluidized bed reactors yield organic condensibles which are normally in the lower part of the range while updraft gasifiers produce tars at the higher end of the scale.

The condensate, therefore, which combines both the water

TABLE 1

Organic Components Present in Gasifier Condensates

Acyclic Hydrocarbons	
Propane	Propylene
Butane	Butene
Pentane	Pentene
Cyclic Hydrocarbons	
Benzene	Methyl Acenaphthylene
Toluene	Anthracene
Xylene	Methyl Anthracene
Methyl Styrene	Benzo α Anthracene
Biphenyl	Phenanthrene
Naphthalene	Methyl Phenanthrene
Methyl Naphthalene	Pyrene
Dimethyl Naphthalene	Benz α Pyrene
Phenyl Naphthalene	Indene
Acenaphthylene	Fluorene
Acenaphthene	Fluoranthene
Heterocyclics	
Benzo Furan	Dibenzo Furan
Dibenzo Pyran	
Carboxylic Acids	
Formic Acid	Acetic Acid
Propionic Acid	Isobutyric Acid
Butyric Acid	
Aldehydes/Ketones	
Acetone	Methyl Ethyl Ketone
Furfural	Fluorenone
Acyclic Alcohols	
Methanol	Ethanol
Cyclic Alcohols	
Phenol	Resorcinol
o-Cresol	Hydroquinone
m/p-Cresol	α Naphthol
Dimethyl Phenol	Hydroxy Fluorene

and the organic material, comprises a predominantly aqueous mixture containing 0.3 to 40% of carbonaceous liquids. This range is somewhat extreme and it is more normal to find levels of 1 to 10% or 10,000 to 100,000 mg/litre with individual components being present in amounts varying from traces to 10,000 mg/litre.

Of specific interest are the environmental properties of the condensate. If it is assumed from the data of Duncan (1981) that the organic material can be represented by the empirical formula of $CH_{1.06}O_{.21}$ then the chemical oxygen demand (COD) is approximately twice the organic concentration i.e. 20,000 to 200,000 mg/l. The five day biochemical oxygen demand (BOD_5) is typically one half of the COD level or 10,000 to 100,000 mg/l. For comparison, the standard limits for discharge to a sewer system are 250 to 300 mg/l BOD_5, while regulations for introduction into the natural environment limit aqueous discharges to 30 mg/l BOD_5. It is obvious, therefore, that the condensate requires extensive treatment before it can be released to the aquatic environment. In addition to the high oxygen demand, the material contains refractory compounds such as phenols and potential mutagens, Duncan (1981). It is of extreme importance, therefore, that an economical, yet effective, pollution control technology be developed to ensure that gasification can achieve its full potential.

To this end, a variety of new techniques hold promise as treatment methodologies for reducing the pollution from gasification systems. These include advanced biochemical technologies, ultrafiltration, combustion, wet oxidation, and extraction. These processes will be briefly discussed at a later stage in the report. However, there is one potential treatment method which can be used to minimise the effects of the condensate by converting the organic material to gas, principally carbon monoxide and hydrogen, prior to condensation. This technique is steam reformation.

2.3 Reforming Equilibria

In section 2.1, reaction (7) was identified as one of the mechanisms responsible for the decomposition of the condensible organic material. This reaction, employing steam and heat as a means of cracking hydrocarbons, is widely practised in the petrochemical industry and is commonly described as reforming. Most frequently, the technique is used in the presence of a nickel catalyst to decompose naphtha or methane into carbon monoxide and hydrogen for the production of synthesis gas. Henceforth, reaction (7) will also be referred to as reforming.

Reforming is an equilibrium reaction which, at high temperatures (750°C), favours the production of carbon monoxide and hydrogen. Only methane retains some stability

at these temperatures. At lower temperatures (300°C) the equilibrium reverts to hydrocarbon formation, e.g. the Fischer-Tropsch synthesis.

To elucidate the effects of the reforming reaction on the materials found in the organic condensates, a theoretical approach was initially adopted. The procedure, which is described in greater detail in appendix A, involved the calculation of the reforming equilibrium constants (Kp)for many of the materials identified in table I. The van't Hoff isotherm in conjunction with the enthalpy and Gibbs Energy function (F-H)/T were used as the basis for the calculation of Kp for the reforming reaction. The equilibrium constant, Kp, for reaction (7) was defined as follows:

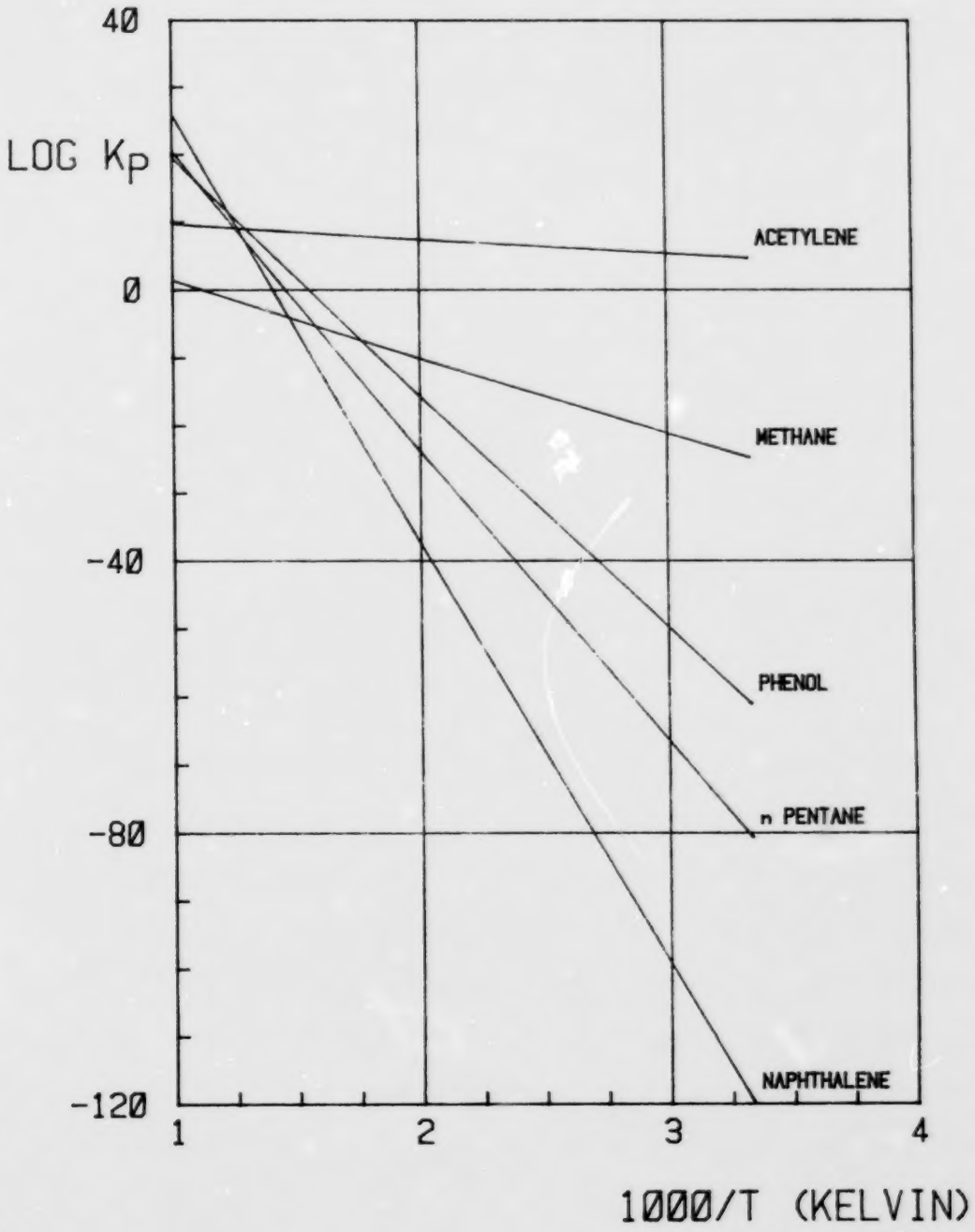
$$Kp = \frac{Y_{CO}^{m} \cdot Y_{H_2}^{m-o+n/2} \cdot P^{m-1+n/2}}{Y_{C_mH_nO_o} \cdot Y_{H_2O}^{m-o}} \qquad .....(a)$$

where Y_i is the mole fraction of component i and P is the absolute pressure of the gas phase (ata). Typical values for Kp as a function of temperature are illustrated in figure 1 and in the appendix (Table A-2).

It is evident from the calculated information that the majority of compounds, with the exception of acetylene and the oxygenates, are reasonably stable up to a temperature of

FIGURE 1

TEMPERATURE VS REFORMING EQUILIBRIUM CONSTANT



about 700°K (427°C). However, all with the exception of methane, have a strong tendency towards decomposition at temperatures of 900°K (627°C) and higher. As might be expected, the higher members of a homologous series are more susceptible to decomposition by reformation at temperatures above 700°K.

In addition to the determination of Kp, the technique was used to estimate the equilibrium concentration of the components of interest over the same temperature range. The concentrations were evaluated at conditions thought to be typical of those occurring in an operating environment, i.e. wet and dry biomass at atmospheric pressure and dry fuel under pressure (20 atmos) - the latter to simulate synthesis gas production. More details of the assumptions used can be found in appendix A. The results of calculations are furnished in figures 2 and 3 and in table A-3.

The information presented, confirms the conclusions previously reached, namely the equilibrium concentrations of organic materials are negligible at temperatures greater than 900°K. Nevertheless the equilibrium values increase significantly as the temperature falls towards 700°K. Because of the simplistic nature of the assumptions, the concentrations at 20 ata, calculated for 700°K, tend to deviate from the true values for many of the compounds. In

FIGURE 2

TEMPERATURE VS EQUILIBRIUM CONCENTRATION

(PRESSURE - 1atm)

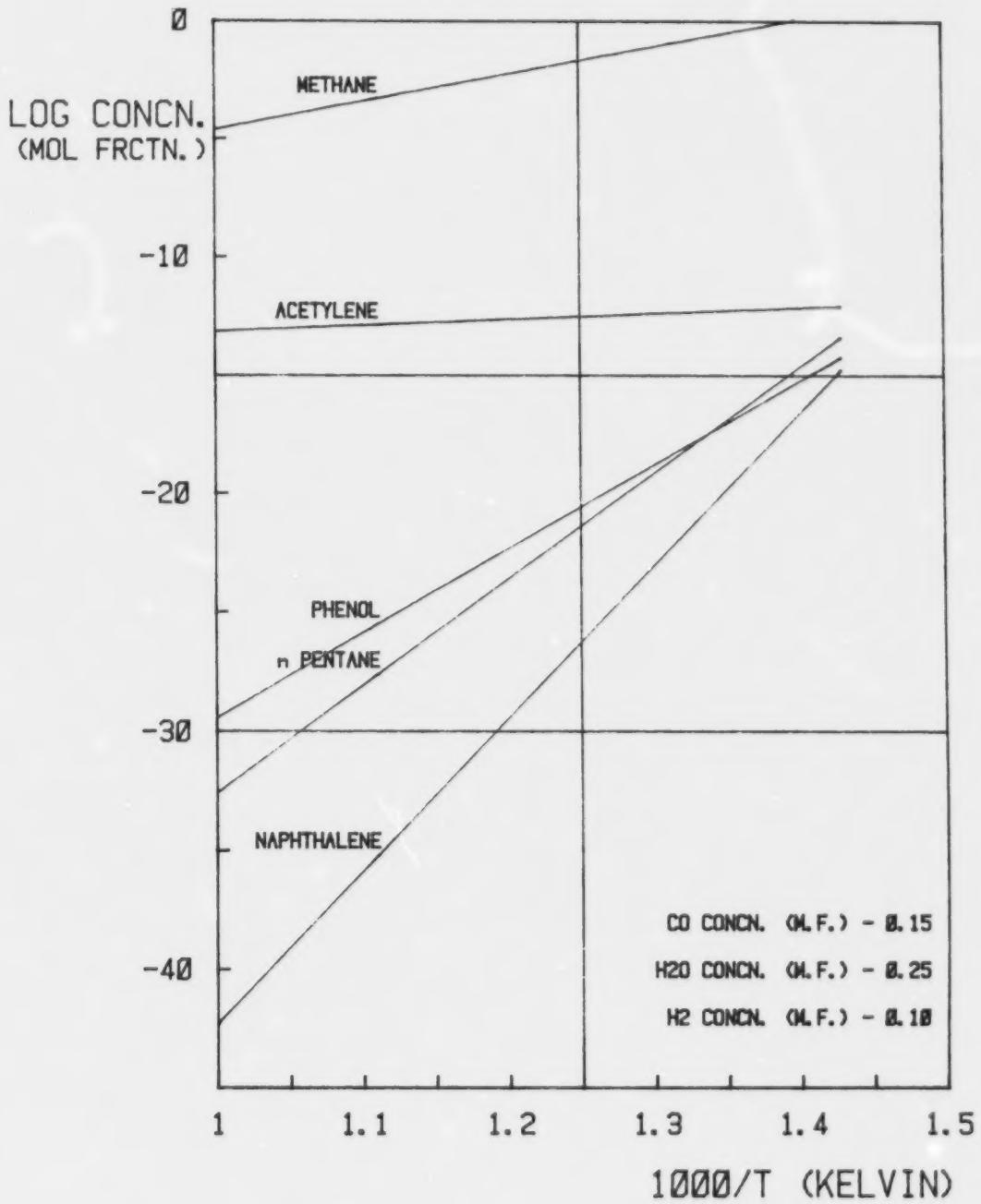
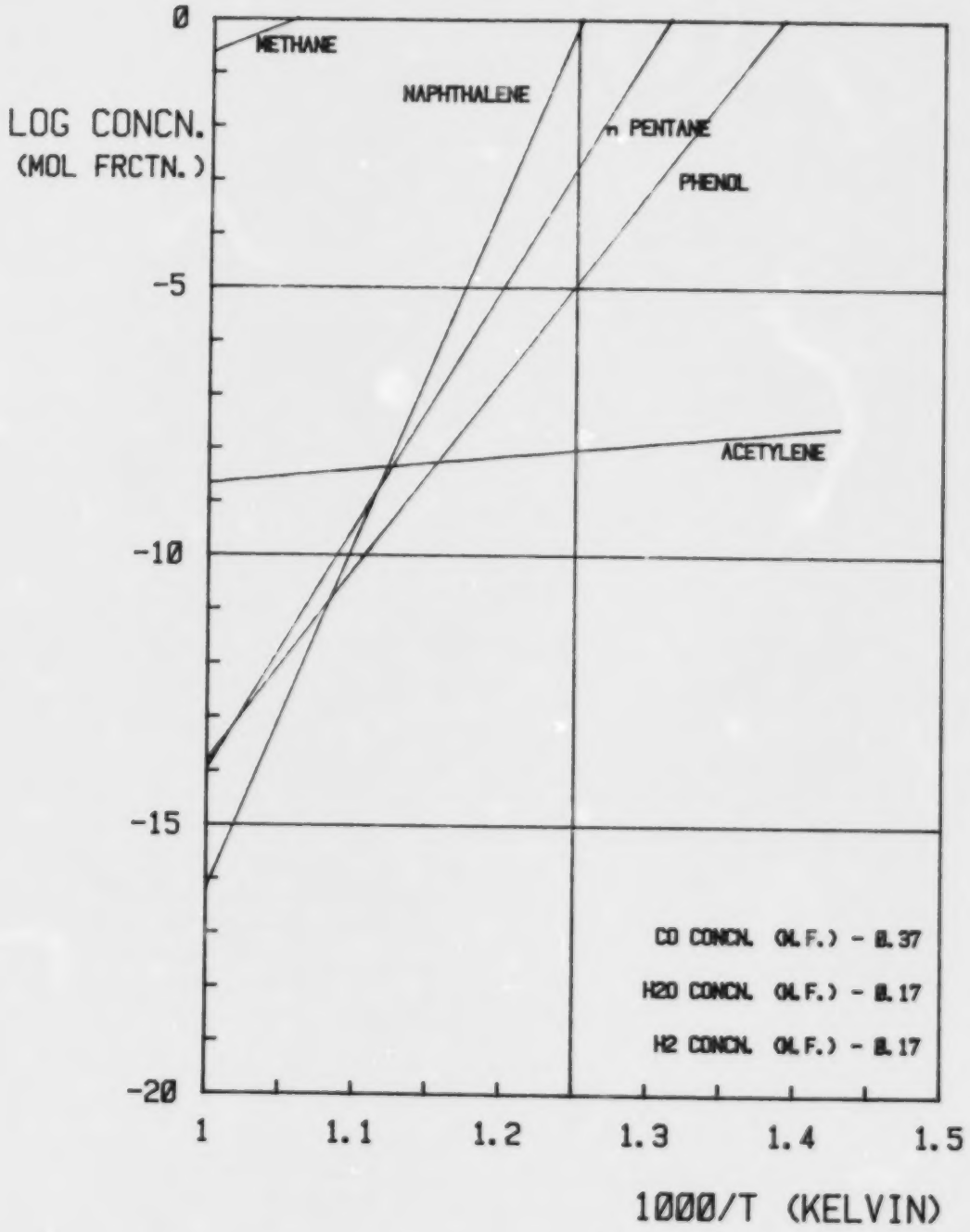


FIGURE 3

TEMPERATURE VS EQUILIBRIUM CONCENTRATION

(PRESSURE - 20atm)



the absence of interactions from other components, it is estimated that the equilibrium concentration of many of the individual materials at 700°K and 20 ata is greater than 1%. There are some exceptions - acetylene and oxygenated compounds.

In summary, if reforming equilibria can be attained, then the concentration of condensible organic materials will be reduced to negligible levels at temperatures above 500°C.

2.4 Reforming Kinetics

The fact that the calculated equilibrium constants for the reforming reaction predict almost total decomposition of the majority of components in the gasifier condensate at temperatures above 500°C, does not necessarily imply that the simple application of heat to the gas will destroy the organic residues. Rather, equilibrium denotes the concentration ratio that would be achieved after an infinite period of time. In many reversible reactions, a very close approach to equilibrium can be attained within commercially viable time spans. This is not the case for conventional reforming of methane or naphtha both of which require catalysts. However, condensate reforming may occur with greater facility.

Reforming dates back to the early 19th century when

catalysts, such as platinum, palladium and nickel were used to decompose olefins. Towards the end of the 19th century calcium oxide was used commercially to produce hydrogen by reforming. Later a broad range of catalyst compositions, British Patent 267535, 1926, was claimed to enhance the reforming reaction. The catalytic ingredients included iron, nickel and cobalt which were activated by oxides of sodium, potassium, magnesium and aluminium. However, nickel achieved pre-eminence and continues to be used as the basis for all commercial reforming catalysts.

The recent work of Antal (1983) provides insight into the reaction rates involved in the decomposition of the condensible organic fraction formed during the initial dissociation of biomass, reaction (1). Antal describes a lumped parameter model which he uses to segregate the cracking process, reaction (6), into two separate sequences involving:

- the production of additional permanent gases
- rearrangement into different condensible components.

In the present program, both the unreacted primary and the secondary condensible materials are under investigation. Antal's work indicates that dissociation of the primary species should proceed readily.

All of the above factors tend to suggest that reforming of the condensible materials produced during gasification should be technically feasible. However, both heat and catalysts will probably be required. Based on earlier work by others, it appears that an initial approach involving catalysts, such as lime, nickel, alumina or alkali oxides, should prove advantageous.

3.0 EXPERIMENTAL PROGRAM

The objective of the experimental program was the identification and quantification of some of the factors affecting the decomposition of the condensible organic material produced during the gasification of biomass. The principal parameters to be studied were temperature and the effect of catalytic materials with a known propensity for the cracking or reforming reactions.

To set up an experimental program such as this, three important decisions are required:

- whether to simulate a typical gasifier product or to utilize the gas from a production gasifier.
- identification of the scale required for meaningful commercial design.
- selection of reactor configuration that will simplify the experimental work and the subsequent engineering design.

As has been described previously, gasifiers produce a very complex mixture of materials many of which have not been identified. As a result, direct simulation is not possible and simulation with model compounds is unlikely to yield meaningful results. Consequently, it was concluded that the test program should be based on the utilization of the

gas directly from an operating system. In turn, this necessitates that the reforming equipment be field mounted with appropriate experimental site support.

Although many commercial reactors have been designed from the results obtained with very modest sized bench scale equipment, this was not thought feasible in the present situation. In this instance, the operating environment involved long feed lines, inclement weather conditions and gas streams notorious for their ability to deposit and coke during unsteady state operations. After consultation with gasifier operating personnel it was concluded that the equipment should be of substantial magnitude with pipelines sized to 25mm or larger and concomitant, high gas velocities. As a result, the reformer was sized to utilize 0.1 to 0.3 m^3/min of gas. Subsequent experience indicates this to have been a wise choice although it is believed that smaller equipment could have been utilized provided that all elements, including pipelines, would have been heat traced at all times to 300°C.

With all of the above conditions imposed on the choice of a reactor system, only two geometries were feasible - packed bed or fluidized bed. Although conventional reforming equipment is of the fixed bed type, there are a number of complications, in terms of kinetic evaluation, which result from fixed bed use. These include temperature gradients,

particulate deposition, and potentially uneven carbon precipitation and poisoning. Fluidized beds on the other hand can provide an isothermal environment and ensure that changes in catalyst activity are evenly distributed throughout the bed while minimising the problems associated with particulates in the gas stream. Fluidized beds, like fixed bed reactors, are not true plug flow systems and back mixing can complicate the analysis of the kinetic data. Consequently, it was conceived that program would consist of two stages

a) Tests with a fluidized bed unit to delineate kinetics, evaluate catalysts and determine other operating problems. The behavioural studies of Yoshida et al (1974), Wen et al (1977), Blake (1979) Coram et al (1979) and Eakman et al (1980) indicate that a kinetic analysis, adequate for preliminary engineering, would be possible.
b) Based on the above tests, a fixed bed reactor would be designed and tested to simulate the long term commercial operating environment and hence evaluate such problems as poisoning and coking.

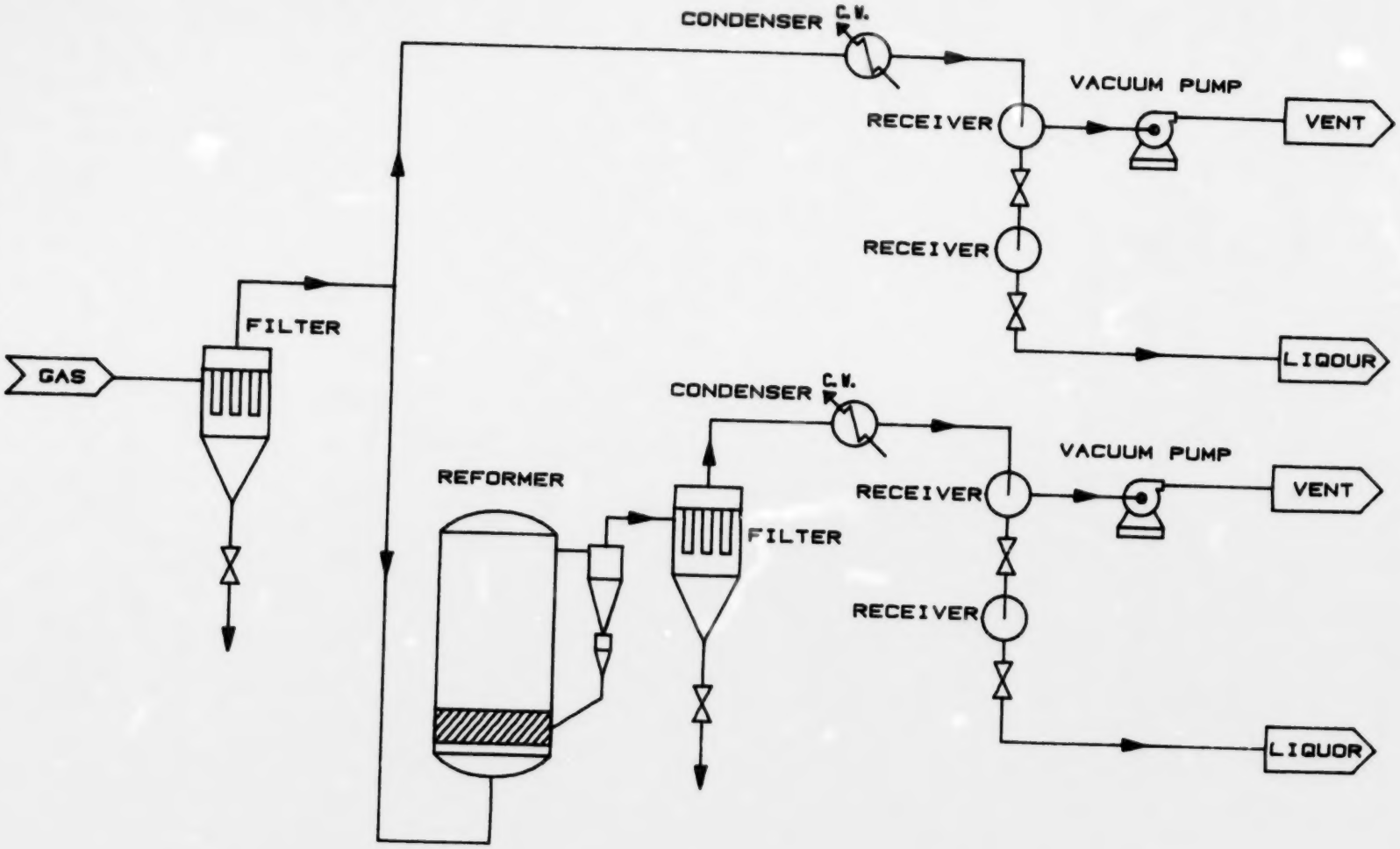
Unfortunately, the latter test was not carried out during the present study because of time constraints.

3.1 Equipment Description

The principal function of the equipment was the determination of reaction rates for the reforming reaction. This entails the measurement of both inlet and outlet concentrations. In the present study, it would have been an extremely difficult, if not impossible, task to identify and quantify each of the components in the gasifier stream. Of necessity, a simpler technique had to be utilized. In this instance, since the ultimate intent of the technology is the reduction of pollution from the condensate, a technique for monitoring this should provide an appropriate measure of the efficacy of the system. Accordingly, COD was chosen as the means of quantification. While this does not permit a detailed mechanistic evaluation, it does allow for comparison of catalyst activities and for subsequent equipment design. Accordingly, the apparatus was engineered around the need to condense a sample of the inlet gas and the reformed gas.

The equipment was constructed as shown in the flow diagram of figure 4. Gas from the gasifier was directed first to a high temperature sintered stainless steel filter fitted with an automatic blowback for cleaning the filter on-line. When required, this filter could be by-passed to evaluate directly the effects, catalytic or otherwise, of the gasifier particulate on the treatment process. Following

FIGURE 4. REFORMER FLOW DIAGRAM



filtration, the gas was split into two streams one of which, the blank, was directed to a condenser, a reflux separator to permit instantaneous liquor sampling, and a receiver. The condensate collected in the container could be discarded to a second vessel while on-line and subsequently discharged. All of the condensing equipment was constructed in glass for convenience of observation. The cooled gas from the receiver was evacuated through a mist separator and a dry test meter by means of a rotary vane pump.

The process stream from the filter was directed to a fluidized bed reactor 150 mm. ID x 3 m. high. The unit was insulated both inside and out and the lower 750 mm. electrically heated. A variety of different heating elements were tested during the project. However only one, a 5kW wall heater with the heating wire imbedded in refractory, proved to be satisfactory. The temperature of the fluidized bed was maintained by a three term controller which regulated the heating element. The bed incorporated a nozzle type distributor, a solids sampling valve and a cyclone return leg. After reaction in the gasifier, the gas was first passed through a cyclone, then a second high temperature metal filter and finally to the liquor condenser, sampler and vacuum pump as previously described for the baseline stream. The process stream was also fitted with a flow control system to maintain constant flow

conditions in the reactor.

In addition to the controls already described, the apparatus included extensive temperature and pressure monitoring equipment as exhibited in figure 5. The measurement loops incorporated both direct read-out and data logging facilities.

The data acquisition system comprised a Hewlett Packard 3497A data logger, a Hewlett Packard 85A micro-computer and a 2.2 megabyte 9895A flexible disc drive. The microprocessor based equipment was used as follows:

- to store all of the instrument data including the output from a gas chromatograph
- to display both the data and the chromatogram.
- to control the operation of the pilot plant including the solenoid operated sample valves, filter backflush, flow control and the GC sequencing.

A summary of the functions is illustrated in figure 6.

The gas chromatograph was a Carle process GC equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID) and was programmed to analyse both the permanent gases and the hydrocarbons through to C_5. The TCD was used to identify the permanent gases, methane and ethylene, while the FID provided the means to monitor

FIGURE 5. REFORMER INSTRUMENT DIAGRAM

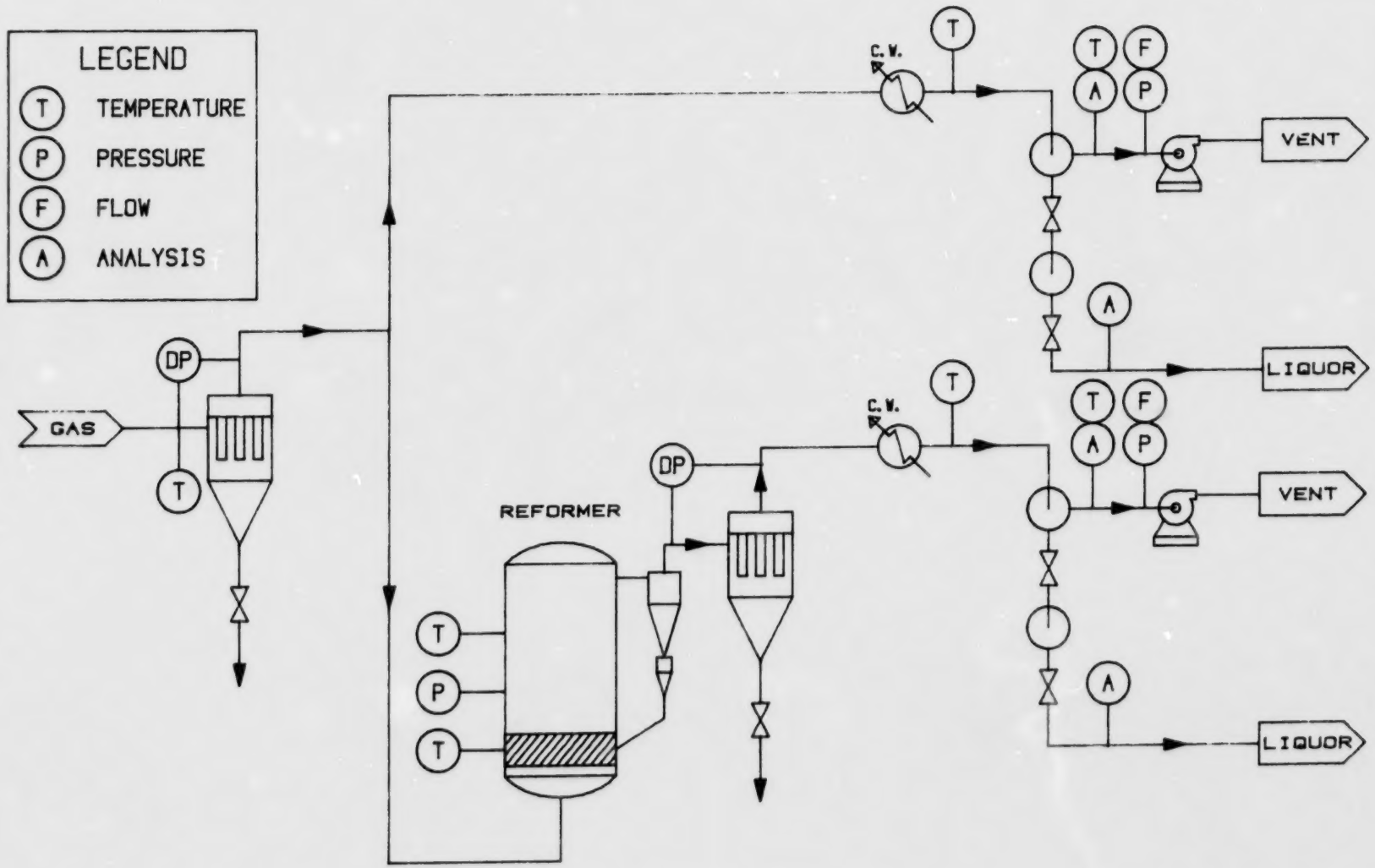
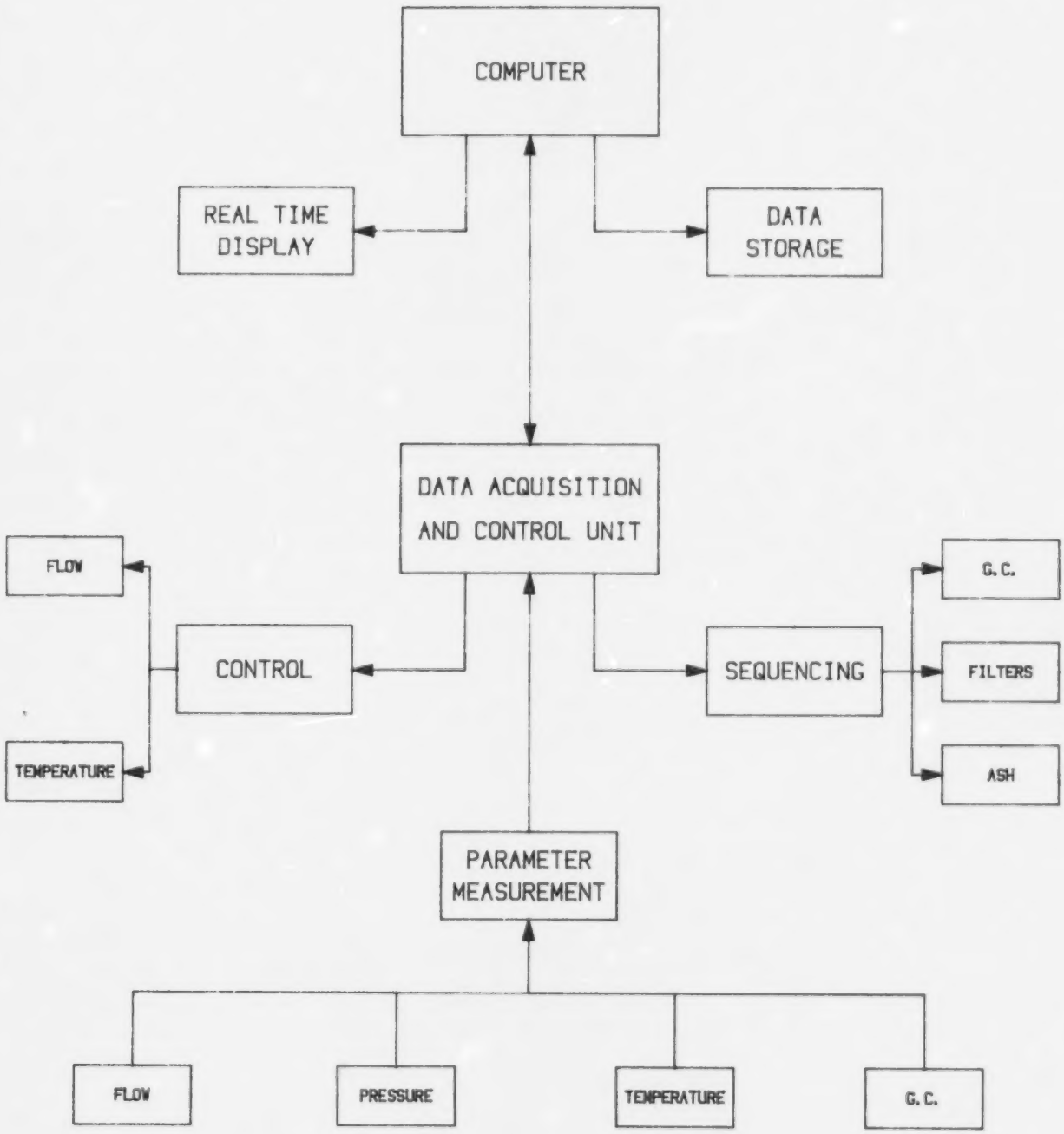


FIGURE 6. SCHEMATIC OF DATA ACQUISITION AND CONTROL



the hydrocarbons. A standard sample of permanent gases and the low molecular weight hydrocarbons, C_1,C_2's and propane, was used for quantification of the gaseous components. The remaining hydrocarbons through to C_5 were determined on the assumption that the FID response was linear with respect to carbon number.

The instantaneous liquor samples were analysed, using standard titration techniques, for COD (chemical oxygen demand). The analyses were carried out by Forintek Canada Corporation.

All of the equipment, with the exception of the condensing section, was electrically traced and insulated. After some experimentation it was determined that, provided the gas streams were maintaned above 300°C, tar deposition was negligible. Accordingly, a set point of 300°C was adopted for control of the heat traced equipment.

3.2 Experimental Procedure

The experimental program proposed for the project entailed the evaluation of certain materials with a proclivity toward the reforming reaction. Catalysts were selected on the basis that their cost would range from readily available inexpensive materials to the more exotic industrial catalysts. It was anticipated that the cheaper materials

would be less active but that perhaps this could be offset by operation at higher temperatures. The range of temperatures thought to be commercially effective for decomposition of the organic condensates was 450° to 850°C. This span was adequate to prevent tar deposition at low temperatures but not too extreme for normal industrial processing.

The specific materials selected for investigation were pure silica sand, limestone, alumina and nickel catalyst (Park Thermal PC-100). The silica sand provided the base material to evaluate background effects due solely to thermal causes. Limestone, one of the early catalysts for the reforming reaction and perhaps the cheapest, was obtained from a local quarry while alumina, which was purchased from Norton Chemical Process and is commonly used as a catalyst support, furnished a material with a high specific surface area. The particular nickel catalyst selected functions conventionally as a cracking agent for methane in reducing gas generators. The properties of the alumina and nickel catalyst are described in Table 2.

Only silica sand had the correct particle size distribution for good fluidization at the gas velocities (0.3 - 1.7 m/s) selected for the test program. All of the other materials required crushing and screening before use. The particle size distribution adopted for testing was -20 mesh,+40

TABLE 2

Properties of Reforming Agents

ALUMINA SA 3232 - NORTON

Chemical Analysis (%)

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O
80.3	27.9	0.4	0.6	0.1	0.2	0.3	0.2

Physical Properties

Apparent Porosity %	Water Adsorption %	Particle Density g/cc	Apparent[(a)] Specific Gravity	Surface Area (m^2/g)
62 - 68	56 - 61	1.0-1.2	3.1 - 3.3	30 ± 5

PARK PC - 100 NI CATALYST

% Nickel	Bulk Density gm/cc	Support	Normal Operating Temp.
7	0.6	Light Weight Refractory	1100 °C

(a) Density of a single porous particle

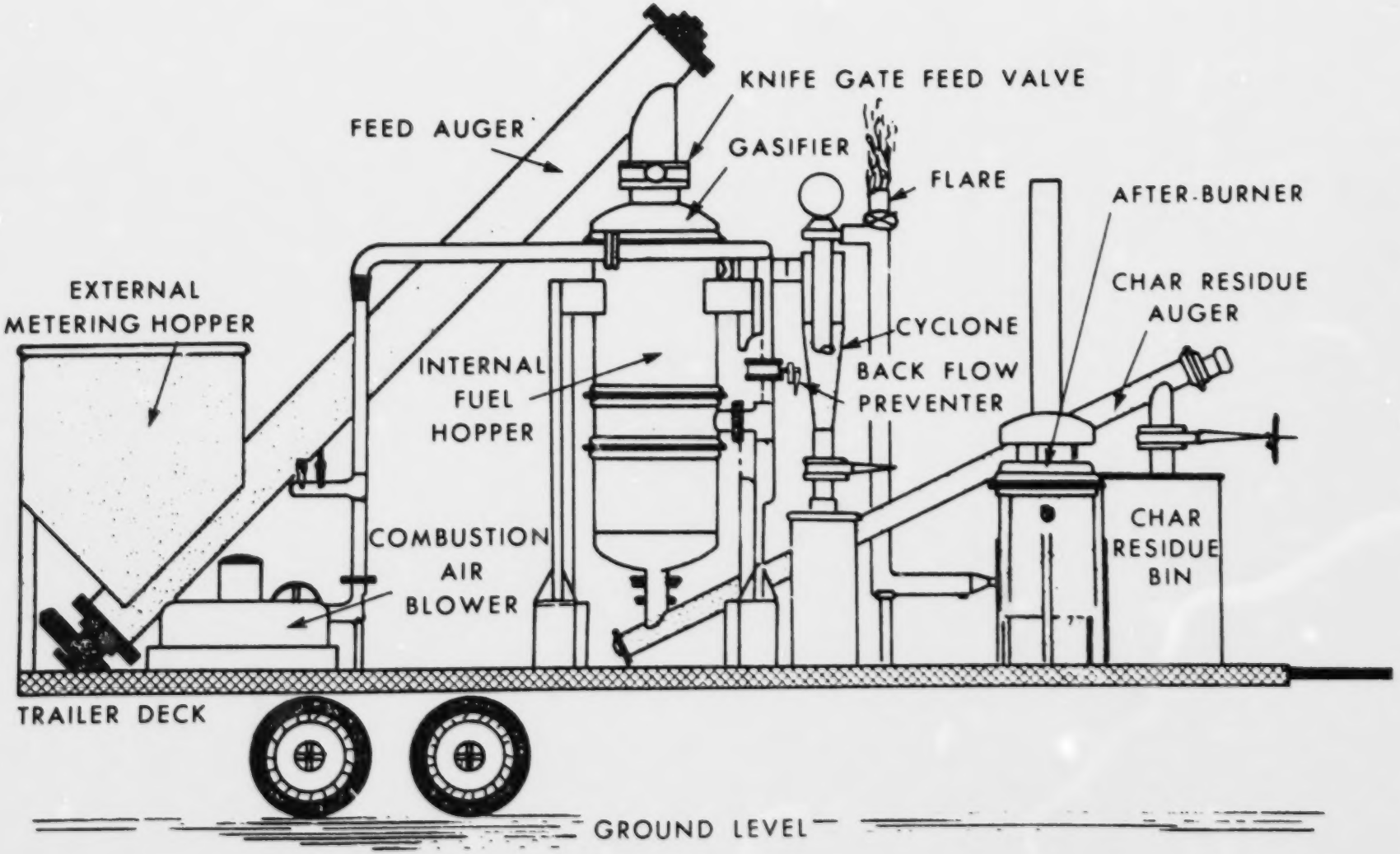
mesh.

Another aspect of the procedure that required early resolution was the identification of the specific gasifier appropriate to both the experimental equipment and the program. Only two choices were possible: the batch fed unit at Forintek Canada Corporation in Ottawa and the commercial Omnifuel gasifier at Hearst. While the continuous gasifier was preferred, it was in a remote location and was not fully operational at the beginning of the test program. As a result, the Ottawa site was chosen as the basis for the tests. This option also made available to the project strong field support through the well equipped facilities and the experienced personnel of Forintek.

The Forintek downdraft gasifier, which is described in detail by Graham et al (1981) and is schematically shown in figure 7, was operated throughout the test program in a batch mode. Fuel, comprising air dried poplar chips, was fed to the gasifier every 20 to 30 minutes. A continuous gas sample was extracted at the gasifier cyclone outlet and piped without further treatment to the reformer.

The specifics of the final operating procedure, adopted after some experimentation particularly subsequent to some difficult winter operations, were as follows:

FIGURE 7. SCHEMATIC OF THE PILOT DOWNDRAFT GASIFIER



- load catalyst into the reformer
- open the air inlet and adjust the pump flow.
- start up the gasifier
- bring the systems to operating temperature.
- standardize the gas chromatograph.
- switch the data logging equipment to automatic.
- divert the gas to the reformer.
- equilibrate the reformer.
- carry out test and sampling procedure.
- switch the reformer to air.
- after one hour shut down system and drain all liquids.

4.0 RESULTS

After some equipment modifications were made to achieve consistency during early 1982, the final tests were conducted in August through October 1982. With the exception of temperature and bed material, the experiments were made under essentially the same conditions. Typical values for the operating parameters are shown in Table 3.

As might be anticipated with an unprotected facility, there was some variability in the gasifier operating conditions, primarily due to weather. It was noted that during rainy periods, the tar loading tended to increase by about 10% or more. While this is insufficient to affect the validity of the data, it presumably increases the data scatter.

A second operating problem was encountered due to the batch nature of the gasifier. Approximately every 20 - 30 minutes, the unit was shut down, wood added and the gasifier restarted. Although the discontinuity lasted less than 1 minute, it was observed that the condensate colour and concentration changed between interruptions. During the first five minutes after restart, the change was quite pronounced. Consequently, the gasifier was allowed to stabilize for about 15 minutes or more before the condensate sample was taken. Unfortunately the GC was on a programmed cycle of 29 minutes and it was not possible, due to gasifier

TABLE 3

Typical Operating Conditions

Program Temperature (°C)	600	735
System Flows (Nm^3/min)		
Reactor Flow	.184	.185
System Temperatures (°C)		
Inlet Gas	293	273
Reactor in Bed #1	596	735
Reactor in Bed #2	597	734
Reactor Bed Surface	604	712
Reactor Above Bed	543	663
Gas Exit	470	579
Condenser Inlet	167	174
Condenser Outlet	23	21
Flow Meter Inlet	22	20
Condenser Outlet - Bypass	19	20
Flowmeter Inlet - Bypass	20	20
System Pressure (kP)		
Distributor Pressure Drop	6.97	6.48
Bed Pressure Drop	2.98	2.89
Filter Pressure Drop	17.4	18.7
Pressure at Reactor flow meter (absolute)	73.8	73.1
Pressure at Bypass flow meter (absolute)	101	102
Condensate Flows (l/h)		
Reactor Condensate	0.47	0.51

mishaps (bridging etc.), to maintain the GC in the same sequence as the condensate sampling. Hence the GC analyses show considerable disparity, with occasional oxygen concentrations being as high as 25%. Such a sample was presumed to have been taken during the period the gasifier was being loaded. As a result much of the GC data had to be discarded.

4.1 Condensate Results

During the initial tests, it was noted that the condensate samples tended to oxidise quite rapidly within the 48 hour period following the test. Accordingly, air was eliminated from the sample by completely filling the sample bottle and delivering it to the laboratory for dilution and stabilization within 4 hours.

After the evaluation of different analytical procedures, it was concluded that analysis by chemical oxygen demand (COD) provided the simplest technique and was easily reproducible. This method was therefore used as the basis for measuring the organic concentration of the condensate.

The results of condensate analysis for the various runs are summarized in tables 4,5 and 6 and in figure 8.

TABLE 4

Effect of Temperature on Condensibles - Sand

Bed Material	Silica Sand
Particle Size	20-40 mesh
Bed Pressure	92.4 kPa
Bed Weight	10.4 Kg.
Gas Flow	0.19 $Nm^3/min.$

Untreated Gas Condensate COD mg/l	Treated Gas Condensate COD mg/l	Bed Temperature °C
35,200	27,200	483
46,200	10,940	711
45,200	6,870	721
46,900	8,560	737
41,900	5,520	755
40,700	4,780	772
40,100	4,700	798
35,600	6,370	805
29,200	4,430	838
34,700	2,840	854
33,500	3,020	864

TABLE 5

Effect of Temperature on Condensibles - Limestone

Bed Material	:	Limestone
Particle Size	:	20-40 mesh
Bed Pressure	:	80-90 kPa
Bed Weight	:	4.7 Kg.
Gas Flow	:	0.17 Nm^3/min.

Untreated Gas Condensate COD mg/l	Treated Gas Condensate COD mg/l	Bed Temperature °C
44,100	4,680	458
45,000	3,710	666
--	2,930	760
--	1,020	760
--	1,420	810
37,600	1,050	816
	1,400	833

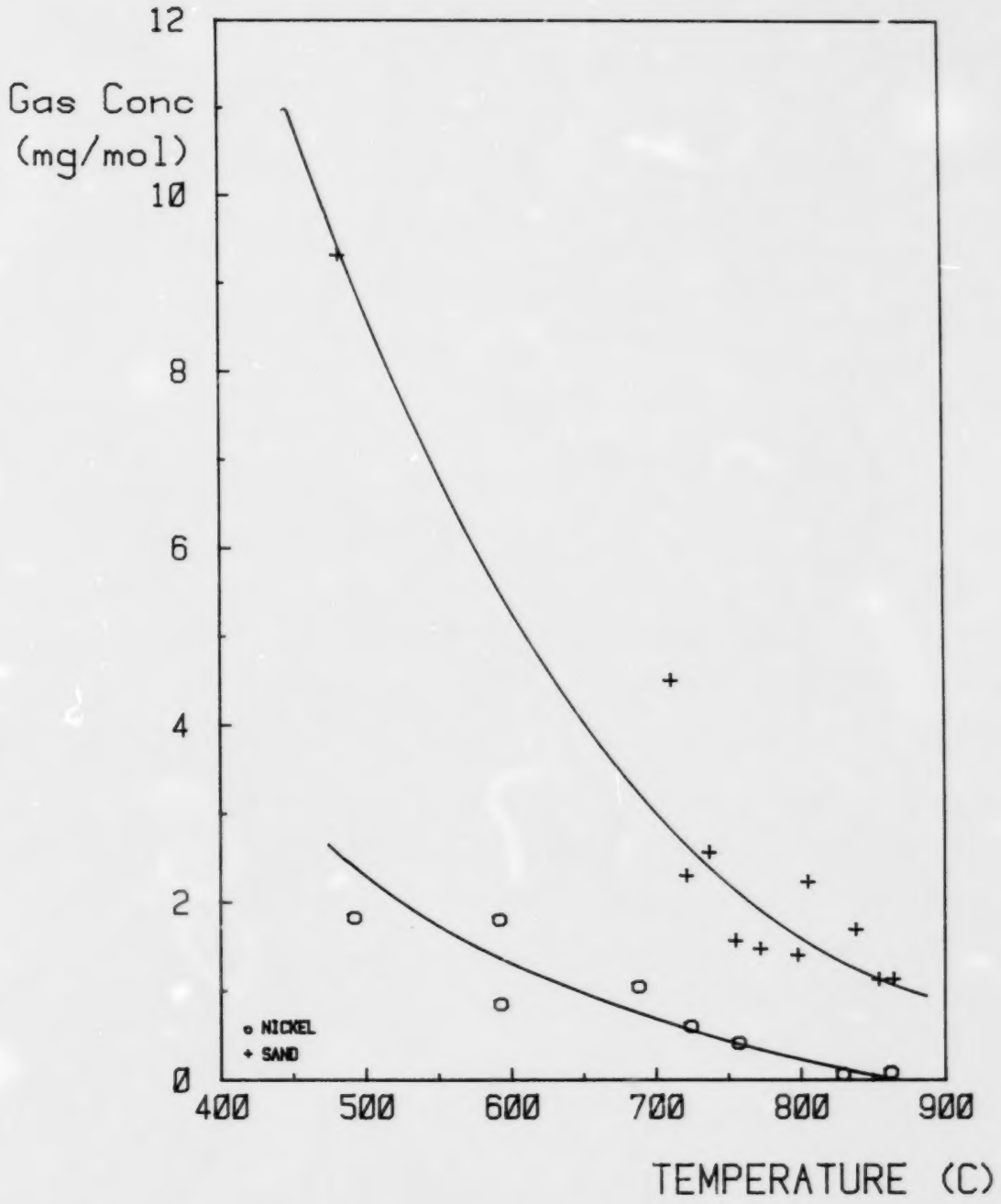
TABLE 6

Effect of Temperature on Condensible - Alumina and Nickel

Bed Material			
Alumina 3 Kg. of 8-40 mesh 20-40 Mesh Ni. Cat.		Nickel (2%) Alumina + 1.2 Kg. of	
Temperature °C	Condensate COD mg/l	Temperature °C	Condensate COD mg/l
510	4,050	492	4,740
--	--	592	5,010
--	--	593	2,220
677	2,980	688	2,940
--	--	724	1,620
760	1,330	757	1,080
804	1,060	829	320
843	1,100	862	360

FIGURE 8

TEMPERATURE VS CONDENSIBLES CONCENTRATION



During the runs with alumina and nickel, the pump evacuating the baseline sample failed repeatedly. Although there was sufficient pressure in the gasifier to blow the gas through the system, it was not adequate for collection of liquor samples. Consequently there are no reformer inlet analyses for these runs. However, the conditions during these runs were very similar to certain of the limestone tests which were carried out under identical weather conditions during the same 48 hour period. These specific limestone liquor analyses were therefore deemed applicable to the alumina and nickel tests.

4.2 Gas Analyses

Continuous samples of the gas stream were withdrawn from the system after the gas had been cooled and the liquors condensed. The samples were evacuated through a stainless steel line leading to the GC. This line was heat traced to prevent possible condensation of water etc. The gas to the GC contained a variety of gaseous components with concentrations ranging from parts per billion to as much as 50%. The GC columns used in the analysis had been selected to measure and quantify both the permanent gases and hydrocarbons through to C_5. Hydrocarbons, C_6 and higher, were collected as a single C_6^+ sample. This particular arrangement enabled the principal gaseous components to be

easily identified and to be quantitified by computer calculation of the peak area.

Most, if not all of the C_1 - C_5 hydrocarbons were identified in the untreated gas sample which is typified by figure 9. However, two additional peaks were observed but not identified. These peaks had similar elution times to iso-Butane and n-Pentane respectively but were much broader. The unidentified compounds were persistent and would bleed through even after all other gases had been purged. As a result, they were thought to be either aromatic or oxygenated materials.

Results of the GC analyses are described in tables 7, 8 and 9 and in figure 10.

TABLE 7

The Effect of Limestone on the Volatile Hydrocarbons

Catalyst	Untreated (Blank)	Limestone	Limestone
Temperature °C	250	675	840
Condensate Concentration COD mg/l	45,000	3,710	1,200
Component	Concentration (mole %)		
[a] Heavies C_6^+	.060	.049	.055
Methane	2.36	2.67	2.66
Ethylene & Ethane	.46	.42	.46
Propane	.0071	.0018	.00022
Acetylene	.025	.025	.016
Propylene	.043	.013	.0036
Propadiene	.0012	.0004	.0004
n-Butane	.0033	.0024	ND [b]
Butene-1	.0024	.0002	ND [b]
Trans-Butene-2	.0043	.00057	.00048
Cis-Butene-2	.0089	.00209	.0015
1,3 Butadiene	.000053	.000009	.000020
n-Pentane	.00019	.00001	ND [b]
Pentenes	.00022	.000014	ND [b]
Hydrogen	13.6	12.6	16.9
Carbon Dioxide	11.9	10.5	10.9
Oxygen & Argon	1.56	1.86	.92
Nitrogen	48.4	48.9	41.6
Carbon Monoxide	16.0	17.7	20.4

[a] evaluated as C_6

[b] ND - not detected, i.e. < .00001%

TABLE 8

The Effect of Nickel Catalyst on the Volatile Hydrocarbons

Catalyst	Untreated	Nickel	Nickel	Nickel
Temperature °C	250	602	690	826
Condensate Concentration COD mg/l	45,000	3600	2940	320
Component	Concentration (mole %)			
[a] Heavies C_6^+	.06	.040	.077	.030
Methane	2.36	2.31	2.31	1.91
Ethylene & Ethane	.46	.209	.302	.205
Propane	.0071	.0015	.0024	ND [b]
Acetylene	.025	.00096	.0018	.0017
Propylene	.043	.012	.015	.0008
Propadiene	.0012	ND [b]	ND [b]	ND [b]
n-Butane	.0033	ND [b]	ND [b]	ND [b]
Butene-1	.0024	.00018	ND [b]	ND [b]
Trans-Butene-2	.0043	ND [b]	ND [b]	ND [b]
Cis-Butene-2	.0089	ND [b]	ND [b]	ND [b]
1,3 Butadiene	.000053	.00067	ND [b]	ND [b]
n-Pentane	.00019	ND [b]	ND [b]	ND [b]
Pentene	.00022	ND [b]	ND [b]	ND [b]
Hydrogen	13.6	14.4	11.7	14.08
Carbon Dioxide	11.9	9.57	11.2	11.6
Oxygen & Argon	1.56	1.1	1.05	.76
Nitrogen	48.4	47.8	49.5	48.4
Carbon Monoxide	16.0	20.1	18.8	18.3

[a] - evaluated as C_6

[b] ND - not detected, i.e. < .00001%

TABLE 9

Comparison of Catalytic Activities at 700°C

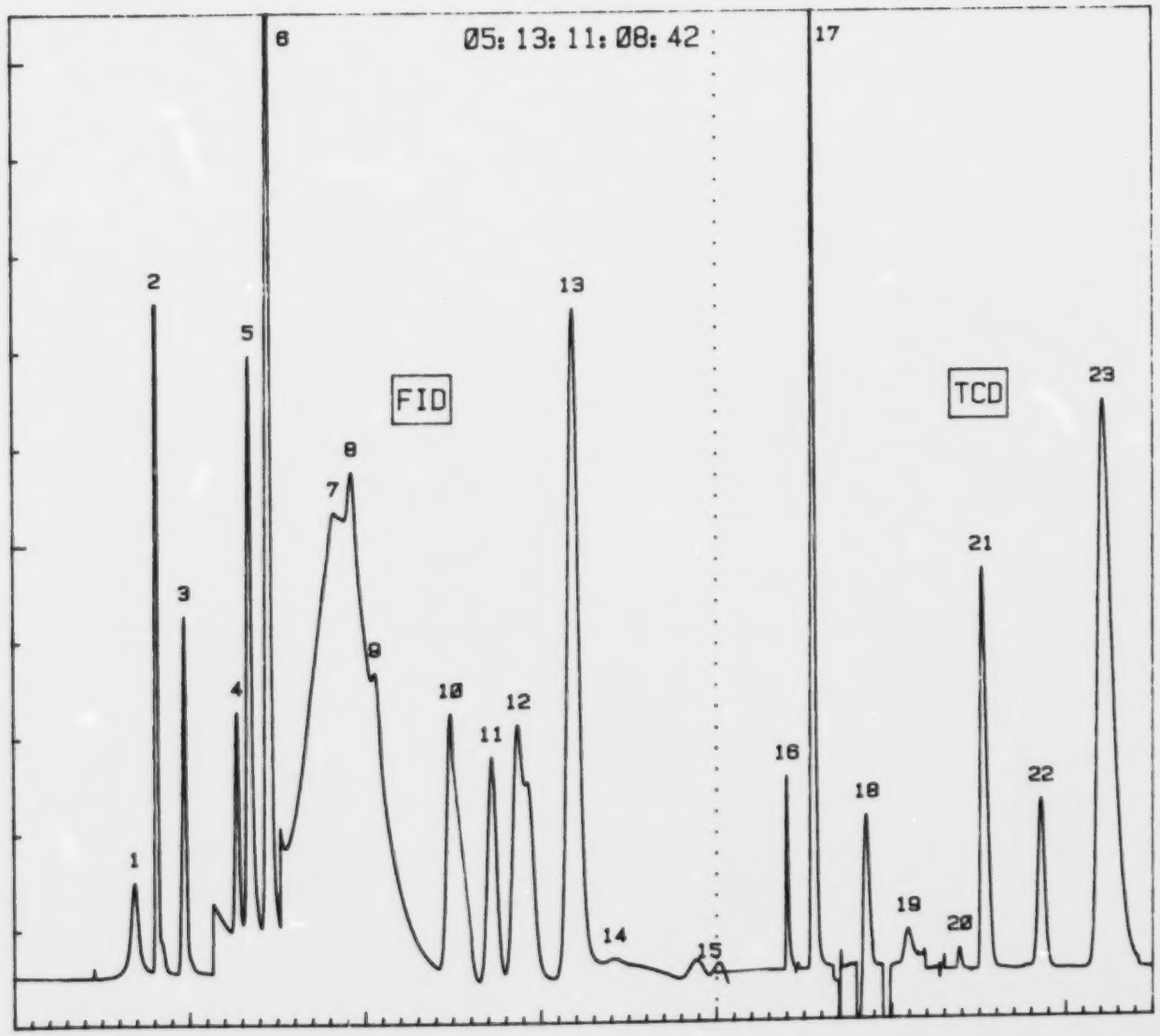
Catalyst	Untreated	Thermal	Limestone	Nickel
Temperature °C	250	706	675	690
Condensate Concentration COD mg/l	45,000	9,500	3,710	2,940
Component	Concentration (mole %)			
[a] Heavies C_6^+	.06	.071	.049	.077
Methane	2.36	3.32	2.67	2.23
Ethylene & Ethane	.46	.74	.42	.302
Propane	.0071	.0034	.0018	.0024
Acetylene	.025	.026	.025	.0018
Propylene	.043	.034	.013	.0015
Propadiene	.0012	.00035	.0004	ND [b]
n-Butane	.0033	ND [b]	.0024	ND [b]
Butene-1	.0024	ND [b]	.00020	ND [b]
Trans-Butene-2	.0043	ND [b]	.00057	ND [b]
Cis-Butene-2	.0089	ND [b]	.00209	ND [b]
1,3 Butadiene	.000053	.000013	.0000019	ND [b]
n-Pentane	.00019	.000012	.00001	ND [b]
Pentene	.00022	ND [b]	.000014	ND [b]
Hydrogen	13.6	[c]	12.6	11.7
Carbon Dioxide	11.9	[c]	10.5	11.2
Oxygen & Argon	1.56	[c]	1.86	1.05
Nitrogen	48.4	[c]	48.9	49.5
Carbon Monoxide	16.0	[c]	17.7	18.8

[a] Evaluated as C_6

[b] ND - not detected, i.e. < .00001%

[c] Sample lost - leaking G.C. valve.

FIG. 9 TYPICAL GAS CHROMATOGRAM



1 HEAVIES
2 METHANE
3 ETHYLENE+ETHANE
4 PROPANE
5 ACETYLENE
6 PROPYLENE
7 ISO-BUTANE
8 PROPADIENE
9 n-BUTANE
10 BUTENE-1
11 TRANS-BUTENE-2
12 CIS-BUTENE-2
13 1,3-BUTADIENE
14 n-PENTANE
15 PENTENES
16 HYDROGEN
17 CARBON DIOXIDE
18 ETHYLENE
19 ETHANE
20 OXYGEN
21 NITROGEN
22 METHANE
23 CARBON MONOXIDE

FIG. 10a GAS ANALYSIS BEFORE TREATMENT

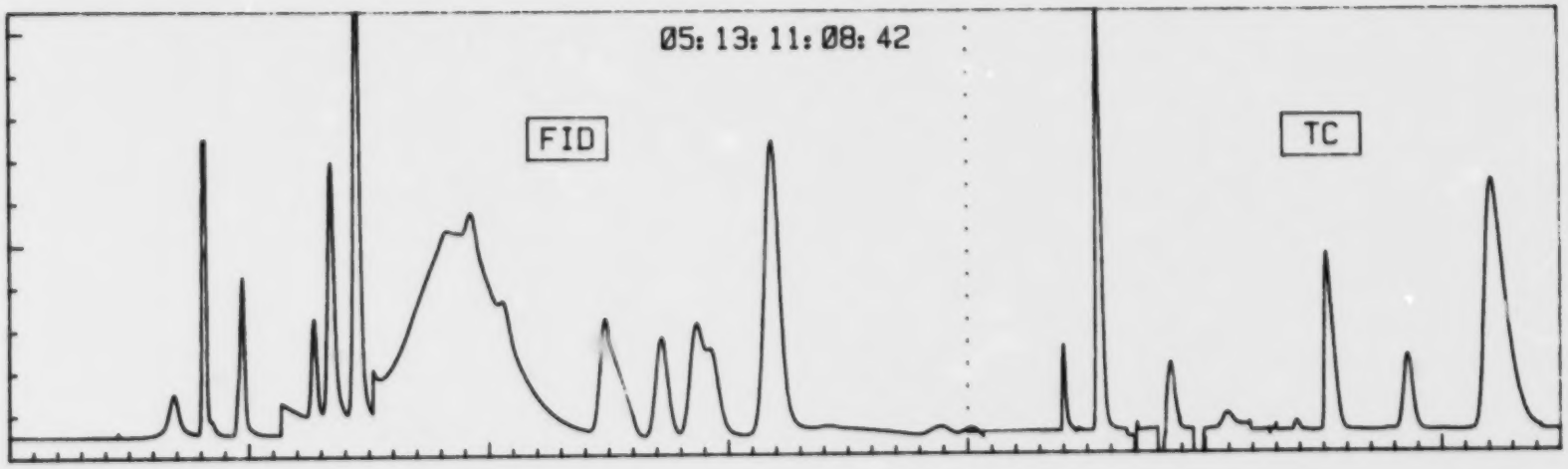
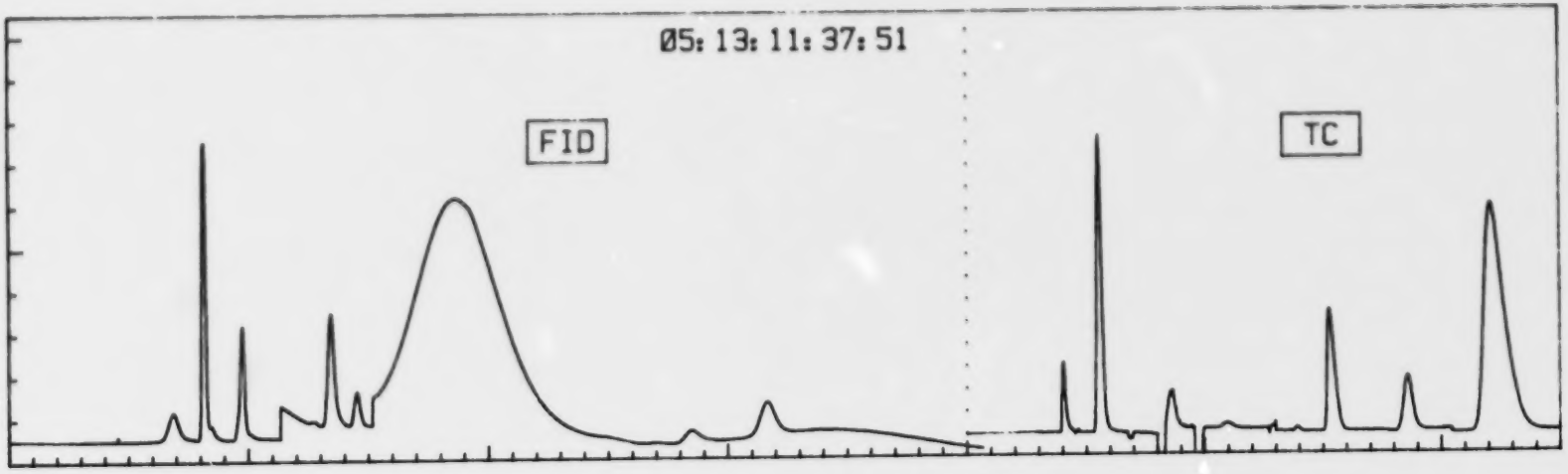


FIG. 10b GAS ANALYSIS AFTER TREATMENT WITH LIMESTONE (840 C)



5.0 DISCUSSION OF RESULTS

The effects of the catalysts are perhaps best segregated into two categories:

- the volatile materials as represented by the GC chromatograms.
- the high molecular weight components corresponding to the condensate sample.

5.1 Effect on Volatile Materials

For the purposes of the present study, "Volatile Materials" will be taken to represent the components that are not condensed from the gas stream at a temperature of about 25°C. This will include compounds which do not condense i.e. where

$$Px_i < p_i \text{ at } 25°C$$

with x_i and p_i being the mole fraction and vapour pressure of species i. Also in the volatile category are materials which do condense but have an appreciable vapour pressure at 25°C. Both classes of materials will furnish a response in the flame ionization detector of the GC. The former category includes the hydrocarbons between C_1 and C_5 as well as a portion of the components identified as C_6^+. The remainder of the C_6^+ fraction represents the vapours of

certain of the condensate compounds.

The gas analysis presented in the Tables 7 through 10 represent only a portion of the chromatograms collected. Many of the data were discarded because of anomalously high oxygen or nitrogen concentrations, i.e. O_2 > 2.5% or N_2 > 55%. In spite of this, there is still considerable data scatter partly resulting from the asynchronous operation of the GC with the batch feeding of the gasifier.

Because of the limited amounts of acceptable data for analysis and the scatter within the data, it is not possible to evaluate the material kinetically. There are, however, some very distinctive trends in the data, perhaps most expressly portrayed in Figure 10. For ease of evaluation, both chromatograms have been partitioned into sections, each segment with different attenuation factors. The attenuation factors are identical for both chromatograms. A visual comparison of the chromatograms indicates that, at this particular condition using limestone as a catalyst at 840°C, most of the hydrocarbon components are significantly affected by the treatment. Only methane, the ethane/ethylene component, the C_6^+ and the unknown peak are relatively unchanged. This is confirmed by the data in Table 7.

Nickel catalyst also exhibits similar behaviour as evidenced by Table 8 and Figure 11. Acetylene, however, appears to

TABLE 10

Comparison of Catalytic Activities at ~830°C

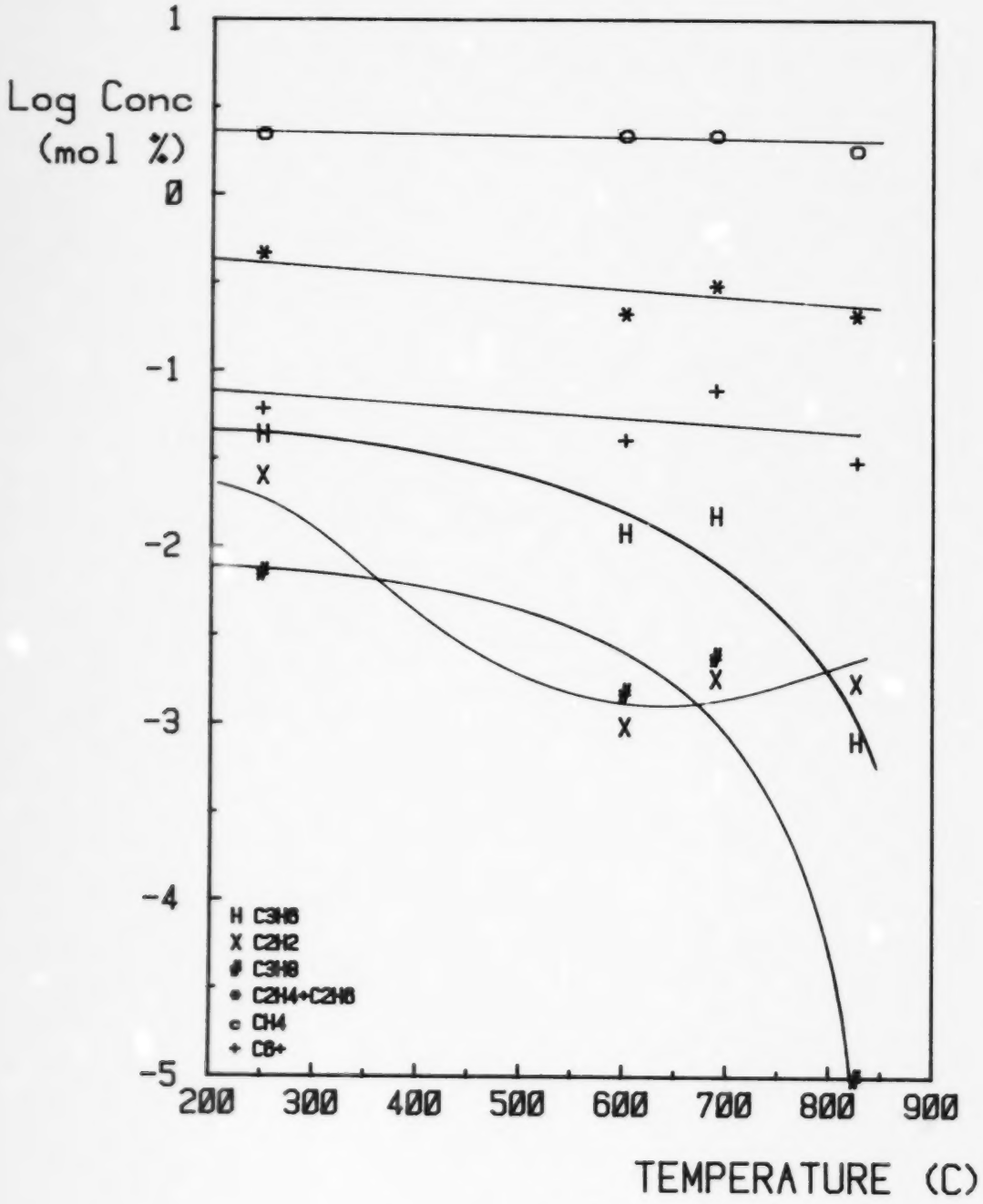
Catalyst	Untreated	Lime-stone	Alumina	Nickel
Temperature °C	250	840	827	826
Condensate Concentration COD mg/l	45,000	1000	1000	320
Component	Concentration (mole %)			
[a] Heavies C_6^+	.06	.055	.063	.030
Methane	2.36	2.50	2.20	1.91
Ethylene & Ethane	.46	.46	.45	.205
Propane	.0071	.00022	.00041	ND [b]
Acetylene	.025	.016	.0175	.0017
Propylene	.043	.0036	.0031	.0008
Propadiene	.0012	.0004	.00034	ND [b]
n-Butane	.0033	ND [b]	ND [b]	ND [b]
Butene-1	.0024	ND [b]	.000002	ND [b]
Trans-Butene-2	.0043	.00048	.00050	ND [b]
Cis-Butene-2	.0089	.0015	.0017	ND [b]
1,3 Butadiene	.000053	.000020	.000030	ND [b]
n-Pentane	.00019	ND [b]	ND [b]	ND [b]
Pentene	.00022	ND [b]	ND [b]	ND [b]
Hydrogen	13.6	16.9	13.3	14.08
Carbon Dioxide	11.9	10.9	11.0	11.6
Oxygen & Argon	1.56	.92	1.05	.76
Nitrogen	48.4	41.6	47.2	48.4
Carbon Monoxide	16.0	20.4	19.0	18.3

[a] evaluated as C_6

[b] ND - not detected, i.e. < .00001%

FIGURE 11

TEMPERATURE VS GAS CONCENTRATION (NICKEL)



be anomalous in that the concentration initially drops but is followed by stabilization or even an increase as the temperature continues to rise. Acetylene and formic acid, it should be noted, are the only chemicals relatively unaffected by the reforming reaction as per the equilibrium constants calculated in Table A-2.

Similar trends are evidenced also with sand (thermal) and with alumina, Tables 9 and 10 respectively. All of the bed materials tend to reduce the identified hydrocarbons containing more than 2 carbon atoms. From a comparison of Tables 9 and 10, nickel is probably the most effective and, within the range of the data scatter, all of the remaining materials exhibit similar activity

Most surprising is the fact that the heavier molecular weight hydrocarbons C_6^+ appear to be relatively unaffected by the catalysts. While this may indeed be the case, another explanation is that the C_6^+ fraction represents mainly the vapours from the condensate. In this instance, the vapour concentration at 25°C would remain constant until the components were sufficiently reformed until they no longer condensed. This would certainly be true for a single compound but this effect may be distorted by the multiple species present in the gas. Although not shown in the data presented, the unknown material is also relatively unaffected by either temperature or catalysts.

The mole concentration of C_6^+ and the unknown materials cannot be directly expressed. However, based on peak areas, i.e. on a weight basis, they each are approximately 1/4 to 1/3 of the methane concentration, or 0.6 - 0.8 wt.%.

One enigma remains: the similarity of the decomposition response among the various fluidized bed media makes it difficult to differentiate whether dissociation of the gaseous components is purely thermal or whether silica sand is effecting a catalytic influence similar to the other bed materials.

In summary, it appears that:

- all of the materials used in the tests effect a significant reduction in the hydrocarbons between C_3 and C_5 over the temperature range from 600 - 850°C.
- In this temperature range, the reduction is more pronounced as the temperature increases.
- Methane, ethylene and ethane, C_6^+, an unknown and possibly acetylene are unaffected within the range of error in the experiments.
- nickel is more active than the other materials.
- the data is insufficient to identify whether the effect is solely thermal or whether sand exhibits a surface active effect similar to nickel, alumina and limestone.

5.2 Evaluation of the Condensate Data

Batch feeding of the gasifier produced corresponding effects on both the condensate flow and concentration, with fluctuations in flow (1:3) and concentration (not measured) occurring in a frequency of 2 to 3 cycles/hr. The potential variability in the data were minimised in this instance by allowing the gasifier to stabilize for 15 minutes before sampling. While this technique may not provide truly representative samples of the gasifier effluent, it does minimise interference effects. The alternative of collecting the total sample over the period and averaging the concentrations would not have permitted evaluation of kinetics other than 1st order. Within this sampling limitation, the following analysis is possible.

First, the raw data obtained from the COD analyses were converted to an equivalent gas phase concentration, expressed as gm/mole of gas. To calculate these, corrections for condensate temperature and gas pressure were applied in conjunction with the assumption that 1 gm. COD was equivalent to 0.442 gms. of organic, through the empirical formula $(CH_{1.06}O_{0.21})_x$ described earlier. The resultant values are shown in Table 11.

Next, an attempt to rationalize the data into kinetic rate constants was made through the following assumptions:

TABLE 11

Gas Concentrations Calculated from Condensate Data

Bed Material	Inlet gms/mole of gas	Outlet gms/mole of gas	Reformer Temperature oC
	.01070	.009314	483
	.01313	.004504	711
	.01058	.002300	721
	.00921	.002563	737
	.01037	.001570	755
Sand	.01020	.001477	772
	.01210	.001407	798
	.00965	.002232	805
	.01017	.001693	838
	.00981	.001133	854
	.01070	.001140	864
	.01210	.002467	458
	.01545	.001131	666
	.01908	.001163	760
Limestone	.01545	.000471	760
	.01545	.000648	810
	.02270	.000410	816
	.01545	.000652	833
	.01004	.001830	510
	.01004	.001449	677
Alumina	.01004	.000646	760
	.01210	.000595	810
	.01210	.000506	830
	.01004	.001891	492
	.01004	.001867	592
Nickel	.01004	.000912	593
	.01004	.001114	688
	.01004	.000668	724
	.01004	.000482	757
	.01004	.000130	829
	.01004	.000151	862

- the reaction is isothermal - true for a fluidized bed environment $\pm 10°C$.
- both radial and axial concentration gradients are absent - not strictly true, but useful for a preliminary evaluation.
- the equilibrium concentration is negligible.
- Steady state exists i.e. the rate of carbon deposition or poisoning is assumed insignificant throughout the runs.
- the reaction is pseudo monomolecular, since other participant reactants are considerably in excess of the condensate concentration. This is true within 5% and hence,

$$r = kC_i^n \qquad \ldots\ldots(b)$$

where r is the rate of reaction, k is a constant, n an exponent and C_i is the concentration of species i.

- the rate is proportional to the total concentration of all condensible species i.e.

$$r = kC^n \qquad \ldots\ldots(c)$$

The final assumption is the most questionable. However, the justification for it rests with the following; there is a large initial diversity of species which is replenished from the intermediate materials produced, and secondly, since the molecules are all large, the dissociation which occurs, particularly on a catalyst surface, most likely takes place one carbon atom at a time. When this is

combined with the observation that the majority of carbon atoms in large molcules behave similarly, the assumption is not too unreasonable.

With these premises, the mass conservation equation reduces to

$$- u \, dC/dZ = r \qquad \ldots\ldots(d)$$

where u is the gas velocity, Z is an equivalent reactor length parameter equal to the length of the reactor in a homogenous reaction and to V_s/A_t in the case of a catalytic reaction (V_s and A_t are the catalyst volume and the reactor cross section respectively). For any specific test, Z is constant, and substituting for r, the equation becomes:

$$- dC/C^n = kZ/u \qquad \ldots\ldots(e)$$

Integrating equation (e) for three typical values of n yields:

1st order (n=1)	$kZ = u \ln C_o/C$	……(f)
2nd order (n=2)	$kZ = u (1/C - 1/C_o)$	……(g)
1/2 order (n=.5)	$kZ = u/2 (C_o^{0.5} - C^{0.5})$	……(h)

The above three values of n were chosen, not from any mechanistic assumption, but to provide the most likely range for n. The values of he parameter (kZ) were calculated for the data in Table 11 for each value of n with the gas

velocity,u, corrected for reactor temperature and pressure.

In conventional laboratory kinetic studies, the value of n would be resolved by varying Z. Because of the nature of the present program, this was not carried out. Instead, the Arrhenius equation

$$\ln k = \ln A - E/RT \quad \ldots\ldots (i)$$

was used in conjunction with a linear regression analysis to identify which of the values of n might provide the best correlation with temperature. The results are summarized in Table 12. The line of best fit is that one with the coefficient of determination closest to 1.

The coefficients of determination do not definitively indicate which of the kinetic equations is the correct one. While second order kinetics do not correlate as well as the others, the data scatter is such that a second order equation could not be ruled out on this basis alone but when combined with the higher improbability of a second order reaction, it becomes justifiable to reject a second order dependency.

A further review of the data, more specifically the activation energy, conveys a similarity of activation energies among the catalysts for the 1st order and 1/2 order reactions but at a very low activation level (<30 MJ/Kg mole). Most catalytic reactions have activation energies

TABLE 12

Regression Analysis of the Arrhenius Equation

Reaction Order	Activation Energy - MJ/Kg. mole (coefficient of determination)			
	Sand	Limestone	Alumina	Nickel
1	56.5 (.945)	19.4 (.906)	23.2 (.950)	26.7 (.890)
2	80.1 (.934)	36.1 (.800)	41.7 (.905)	63.6 (.818)
1/2	47.3 (.926)	16.1 (.953)	18.4 (.956)	16.7 (.936)

greater than 80 MJ/Kg mole. The low values suggest that the reactions may be mass transfer controlled. In fact, if the kinetic constants for sand are divided into two regions, above and below 740°C, the activation energies in each zone are calculated to be 14.2, which corresponds to the values for the catalysts, and 64.5 MJ/Kg mole. This implies the following:

- the reaction rate for reforming in the presence of sand is probably kinetically controlled below 750°C and mass transfer controlled above that temperature.
- the reaction is not homogeneous, i.e. sand is acting as a catalyst.

To confirm the validity of mass transfer control, empirical mass transfer coefficients were evaluated using the model of Kunii and Levenspiel (1969) in conjunction with Froessling (1938) equation

$$\frac{K_d d_p y}{D} = 2.0 + 0.6\ Sc^{.33}\ Re_p^{.33} \quad \ldots\ldots(j)$$

where D is the molecular diffusivity, d_p is the particle size and Sc and Re_p are the Schmidt and the particle Reynolds numbers respectively. On the basis of a molecular formula for the condensibles of $C_{12}H_{13}O_{2.5}$ and bubble sizes of 2 and 4 mm at 500 and 850°C respectively, the following overall mass transfer coefficients were obtained:

Temperature (°C)	k_d (cm/sec.)
500	.934
850	.765

These values lie within the ranges measured by Resnick et al. (1949) for naphthalene, and Kettenring et al. (1950) for water.

If, for comparison purposes, it is assumed that the kinetics of the reforming reaction are diffusion controlled with negligible resistance to the surface reaction i.e. the interfacial concentration can be ignored, then the mass transfer coefficients can be evaluated for each of the condensate samples from the equation

$$Kd = \frac{P_s A_t d_p \phi_s u}{6 W_s} \text{Ln} \frac{C_o}{C} \qquad .....(k)$$

where p_s, W_s and ϕ_s are the density, weight and the sphericity of the solid respectively. Certain of these parameters are not easily measured e.g. particle diameter, sphericity and, in the case of porous materials, the apparent particle density.

For the purposes of calculation it was assumed that the particle size was the average of the screen sizing for the materials, i.e. through 20 mesh and retained on 40 mesh or 0.63 mm. The effective particle density was taken to be

that provided in the manufacturer's specifications, i.e. it was assumed that crushing had no effect on apparent density. The remaining property, sphericity, which is a difficult value to measure, generally ranges from 0.2 to 1 for most solids. Typical values are presented in Table 13. In the present analysis, the estimation of sphericity is further complicated by the fact that two of the materials were porous - alumina and nickel. For this reason, the mass transfer coefficient was not separated from the sphericity. Instead, the parameter $K_d/\emptyset_s$ was calculated as illustrated in Table 14. With allowances for the accuracy of all the assumptions included in the derivation of both the calculated and the measured mass transfer constants, it is not unreasonable to conclude that the values of K_d are sufficiently similar to adjudge that the kinetics of the reforming/dissociation reaction are strongly influenced, if not controlled, by the rate of mass transfer from the vapour phase to the catalyst surface.

Without the benefit of more detailed data it appears logical to develop an empirical correlation, premised on a 1st order rate equation, for a surface reaction limited by the rate of diffusion from the bulk phase to the surface of the catalyst. Hence equation (k) was rearranged to

$$K = \frac{P_s A_t d_p u}{6 W_s} \text{Ln} \frac{C_o}{C} \qquad \ldots\ldots (1)$$

TABLE 13

Particle Sphericity

Material	Sphericity	Reference
Flint sand (jagged)	0.65	(a)
Ottawa sand (rounded)	0.95	(a)
Sand (rounded)	0.83	(a)
Limestone	0.55	(b)
Broken Solids	0.63	(c)

(a) Carman (1937)

(b) Pata et al (1978)

(c) Uchida et al (1934)

TABLE 14

Mass Transfer Coefficients

Catalyst	Mass Transfer Coefficient Kd/Φ_s (cm/sec)	Temperature °C
Sand	.0042	483
	.039	711
	.060	721
	.054	737
	.069	755
	.076	772
	.076	798
	.064	805
	.069	838
	.087	854
	.084	864
Limestone	.118	458
	.205	466
	.238	760
	.345	760
	.329	810
	.354	816
	.331	833
Alumina	.079	510
	.113	677
	.179	760
	.208	810
	.221	830
Nickel and Alumina	.048	492
	.054	592
	.077	593
	.078	688
	.100	724
	.116	757
	.178	829
	.178	862

where K is a constant specific to each of the materials tested. Values for K were solved with the aid of regression analyses to yield the following equation:

$$A.K = .00197\, e^{.0033T} \quad \ldots\ldots\ldots (m)$$

where T is the absolute temperature and A is a constant described in Table 15.

Table 15 Values of A per mole of the Test Material

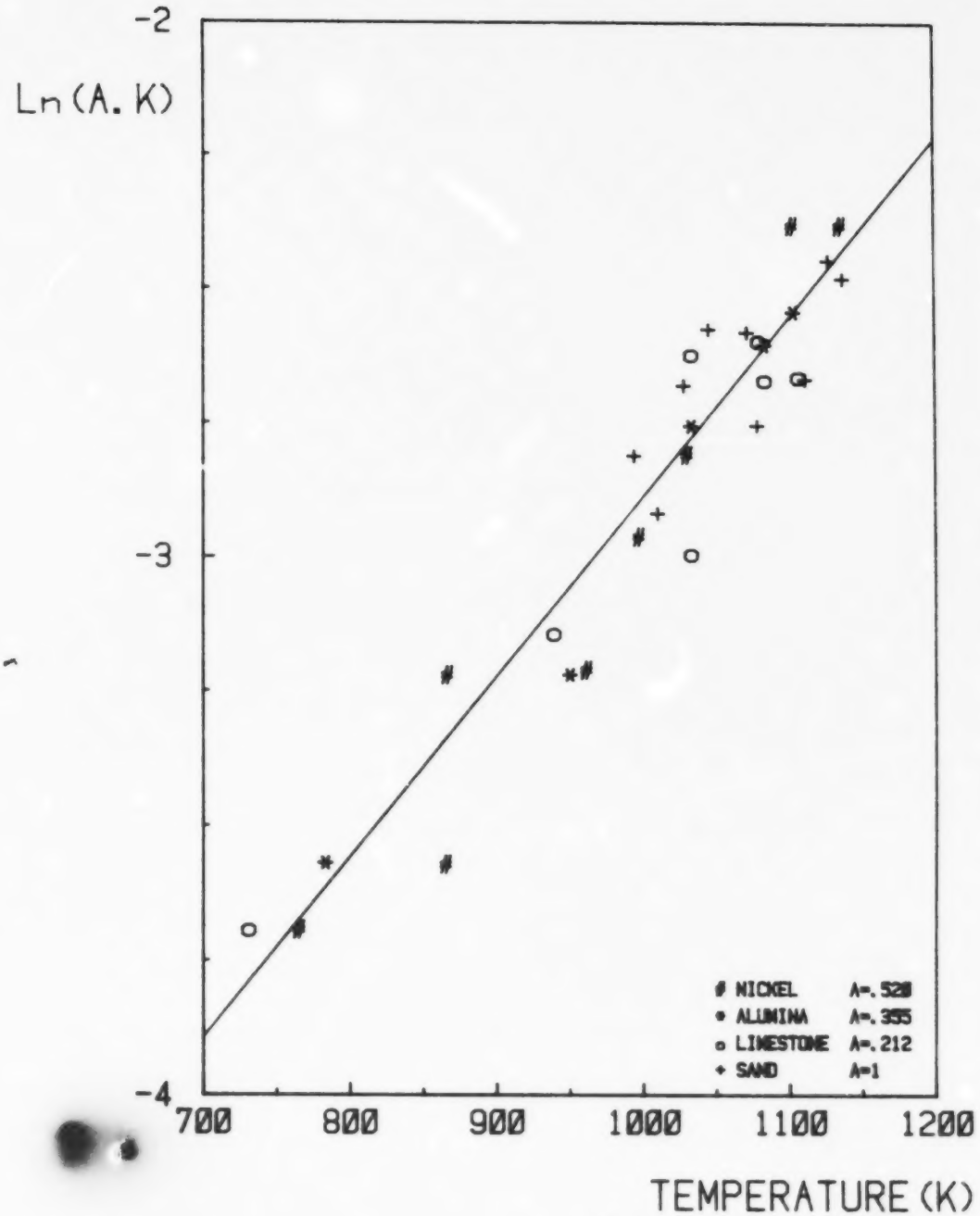
Material	A
sand (above 710°C)	1.000
limestone	0.212
alumina	0.355
alumina & nickel	0.520

The data evaluated in this fashion, are illustrated in figure 12. The coefficient of determination for the equation is 0.92 which tends to support the validity of the analysis presented.

Two data points were not included in the calculation of the values of A. These were the low temperature data points for sand which, as discussed earlier, appear to be anomalous either through a different rate regime or possibly as a

FIGURE 12

NORMALIZED RATE CONSTANT VS TEMPERATURE



result of sampling errors. A review of the sampling procedure and the operating conditions did not furnish any basis for rejection of the data. With consideration given to the rather inert nature of the material, it is therefore not unreasonable to assume that sand provides less of a catalytic effect than the other solids and that, in fact, these data points are valid. Although not shown in figure 12, both data points are considerably below the line of equation (m).

While the constant A could be considered to correspond to sphericity (with the exception of limestone it is generally in the correct relationship) it does include other errors that are lumped together for the purposes of correlation. It should not, therefore, be construed in this way.

Application of equations (l) and (m) should be limited to the specific conditions evaluated during the program i.e. temperatures between 450°C and 870°C (except for sand, 720 - 870°C) and for particle sizes similar to 0.65mm. For particles larger than 0.65mm, the correlation will probably be conservative and vice versa for smaller particles. In the present evaluation, it does not appear to be possible to separate the effect of gas velocity from gas temperature since both are interrelated by virtue of the experimental technique i.e. all of the experiments were conducted with very similar gas flows at N.T.P. In spite of all of the

limitations, the correlation does provide a very useful reference point both for the design of future experimental work and for a preliminary economic analysis.

With respect to comparison of this data with that of other workers, only the studies of Antal (1983) appear to be related to the present experiments. From laminar flow reactor data, Antal developed a kinetic equation to express the dissociation rate of the primary products from the pyrolysis of cellulose. At 450°C and 870°C the reaction rate constant is estimated, from the data of Antal, to be 6.3×10^{-4} and 166 sec^{-1} respectively. To convert the present data to an equivalent reaction rate constant, the values in Table 14 must be multiplied by $6/d_p$ i.e 95. Even in the worst case, sand at 0.4 sec^{-1}, the rate constants are considerably in excess of the Antal data at 450°C while at 870°C the values are 1/3 to 1/10 of the Antal rates. This confirms the fact that all of the materials including sand are acting as catalysts and, from a comparison of the temperature dependency, tends to support the conclusion that the present rates are probably mass transfer limited.

From an evaluation of the condensate data, it appears reasonable to conclude the following:

- Sand, alumina, limestone and nickel all act as catalysts for the reforming reaction.

- Under the reaction conditions examined, 450°C - 850°C, the materials all exhibit a very similar effectiveness except for sand which has a much lower rate at temperatures below 710°C.
- The reaction appears to be diffusion limited at the test conditions, and as a result, temperature has a limited influence on the reaction rate.
- The data obtained can be expressed by the relationship

$$K = \frac{P_s A_t d_p u}{6 W_s} \ln \frac{C_o}{C}$$

where $A.K = .00197\, e^{.0033T}$ (cm/sec)

and the values of constant A are given in Table 15.

- The assumption that the reaction rate is proportional to the total condensate concentration was not invalidated at the conditions tested.

6.0 COMMERCIAL SIGNIFICANCE

To evaluate the commercial viability of any technology, certain key considerations should be assessed. In the present review, three of the more important factors are:

- requirement for a demonstrated need.
- adaptability of the process to conventional construction techniques and operability within normal industrial parameters.
- comparison with other equivalent technologies

The first consideration is directly related to the market demand for gasification processes. In particular, systems involving the fuelling of reciprocating internal combustion engines, the distribution of low BTU gas in a pipeline and the production of synthesis gas, are the most likely candidates for condensate treatment technology.

The renewal of interest in biomass gasification is relatively recent and although the technology has considerable long term potential, current commercial development has been slow partly as a result of world-wide reduction in energy prices and the current economic recession. These negative influences are expected to be short lived and, within the next five years, a pronounced commercialization can be expected. A more definitive

analyses of the market is beyond the scope of the present report.

6.1 Technical Applicability

Many applications, which involve gasification, occur in unsophisticated uses and with mechanically trained operatives. Any add-on technology must therefore incorporate a similar perspective.

Fortunately, the experimental evaluation of the reforming of gasifier condensates revealed some very significant commercial attributes of the process

- System operating temperature is not overly critical with temperatures as low as 500°C being about 1/3 as effective as 850°C. Operating temperatures are, therefore, compatible with most gasifiers.
- The permanent gas composition is relatively unaffected and there is minimal reduction in the heating content of the gas as a result of the treatment.
- Effective treatment of the condensible materials can be achieved within conventionally sized reactors.
- Inexpensive minerals are as effective under the operating conditions as highly refined industrial catalysts.

- The process is relatively simple in operation - not much more complicated than a catalytic converter in automotive use.

The process should therefore be inexpensive and highly operable over the short term. Long term effects, such as catalyst poisoning and particulate problems, were not investigated during the present study. It is anticipated that poisoning effects, if they occur, can be minimised by optimisation of operating temperature and the choice of catalyst, while potential particulate problems can be reduced through appropriate selection of catalyst size, gas velocity and the possible use of fluidized beds.

A cursory review of the technology indicates adaptability to a broad range of gasifier sizes and complexities. Clearly the sophistication of the application will influence the design of the reformer and the ancillaries. To provide a more specific assessment of the operational acceptability of the process, it is useful to examine typical applications.

In its simplest form, such as for automobile or truck use, it is envisaged that the process would treat the exhaust gas from a gasifier by directing the gas through an appropriate length of tubing filled with catalyst pellets. A throw-away cannister using limestone could be readily designed for this application. Also required would be a

simple temperature control device incorporating exhaust gas heat or an air induction valve. A typical equipment arrangement for application to a mobile gasifier is illustrated in Figure 13.

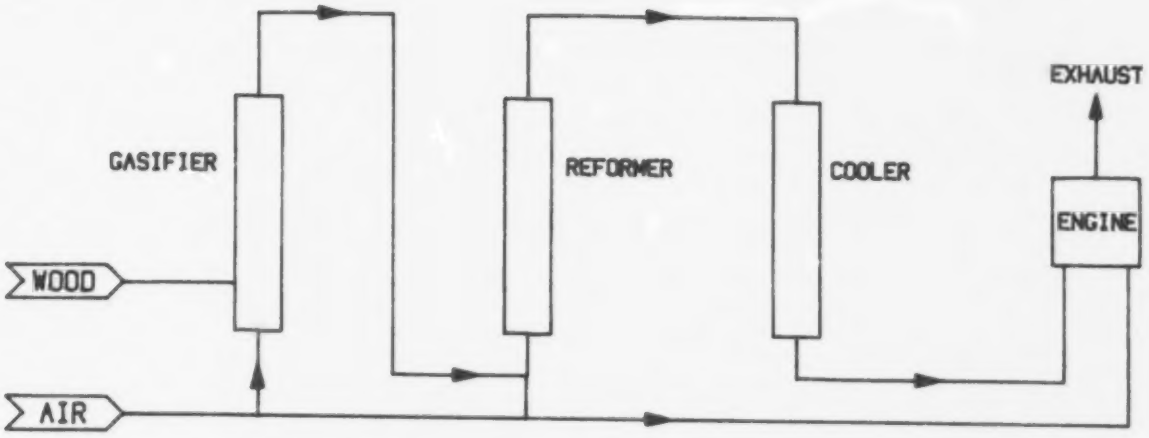
While it is recognized that the automotive application will have little impact in North America, the example is indicative of the lower range of usefulness for the technology and it exemplifies the kind of equipment that must be applied before automotive gasifiers could ever become accepted in a modern society.

More practical applications involve much larger sized gasifiers. In such situations, overall efficiency and downstream equipment longevity become more important requisites. To illustrate the application of reforming to more typical operations, two other examples will be discussed; a downdraft gasifier fuelling a diesel engine and a fluidized bed gasifier producing gas for pipeline use.

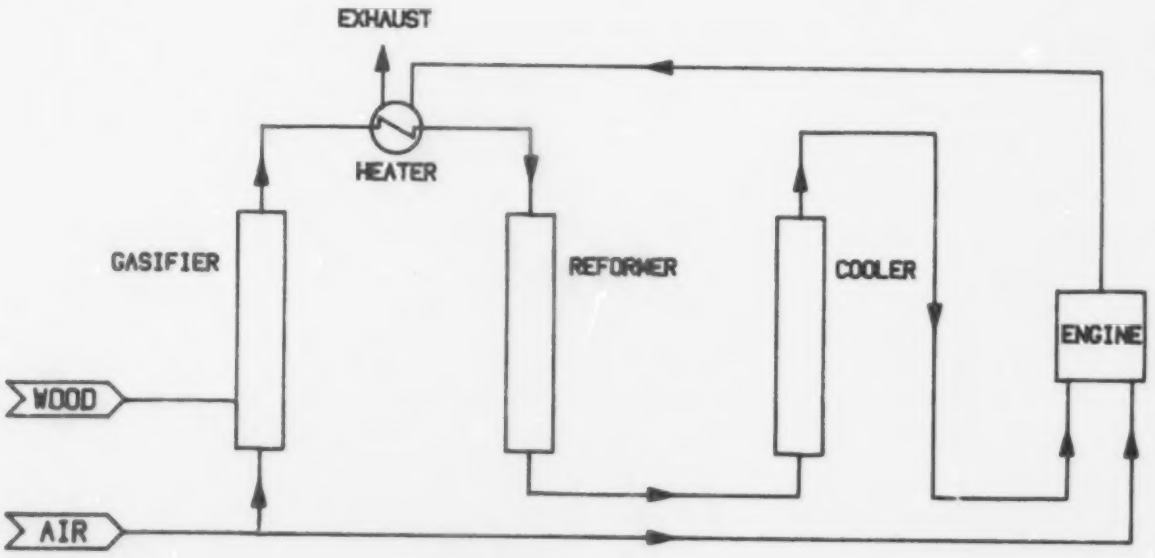
6.1.1 Reactor Considerations

Prior to the review of these specific applications of reforming, it is worthwhile to summarize the requirements for the reforming process, since these are common to both illustrations.

FIGURE 13. AN AUTOMOTIVE GASIFIER WITH A REFORMER



a) Heated by air injection



b) Heated by exhaust gas

6.1.1.1 Operating Temperature

Operating temperature, which is normally quite crucial to most processes, is not particularly critical under the conditions examined in the present study, provided that it is greater than 450°C. This factor is illustrated in Table 16.

TABLE 16

Effect of Temperature on Reactor Size

Temperature °C	450	550	650	750	850
Normalized Reactor Length (Constant Velocity)	1	0.72	0.52	0.37	0.27
Normalized Reactor Length (Constant Diameter)	1	0.82	0.67	0.52	0.42

As is indicated in Table 16, the effect of temperature on the process is two-fold; increasing temperature raises the rate of reaction but also increases gas volume. Normally, the change in reaction rate is orders of magnitude greater than the volume effect. However, because of mass transfer limitations within the present system, increase in temperature from 450°C to 850°C reduces the reactor volume

requirements by only about 60%. Therefore, reactor operating temperature is not critical. Thus the process can be applied to gasifiers which produce an off-gas with temperatures above 450°C without additional heating. This minimises equipment cost. For off-gases less than 450°C, it is probably desirable, without further data, to heat the gas to this temperature. In most cases, there is usually sufficient exhaust heat from the application, i.e. engine exhaust heat in conjunction with an interchanger to minimise the cost of reheating the gas. In the worst situation, injection of small amounts of air will effectively increase gas temperature. The loss in gas heating value is minimal and is offset by the conversion of condensibles to additional combustible gas.

6.1.1.2 Bed Depth

Reactor length is also an important practical parameter, since very long reactors could be cumbersome and expensive. Reactor length is readily calculated from the required outlet concentration. In most instances, since the effluent will ultimately be discharged to a watercourse, a target of 30 ppm COD (about 15 ppm BOD_5) is probably quite acceptable. For discharge to a municipal sewer, 500 ppm COD (250 ppm BOD_5) is satisfactory. Table 17 provides an indication of the length of reactor that is required to

achieve these goals at 650°C.

TABLE 17

Effect of Outlet Concentration on Reactor Size

Catalyst	:	Limestone
Particle Size	:	0.065 cm.
Gas Velocity	:	0.9 m/sec.
Reaction Rate Constant K (A = 0.212)	:	0.195 cm/sec.
Porosity	:	0.5
Inlet Gas Concentration	:	0.017 gms/mole of gas (40,000 ppm COD)
Solids Properties	:	As per Test Conditions
Gas Composition	:	As per Test Conditions

Outlet Gas Concentration (gms/mole of gas)	.00043	.000215	.000013
Outlet COD	1000	500	30
Effective Catalyst Depth (m)	0.36	0.44	0.72

As is illustrated in the table, the catalyst bed depth required to achieve 30 ppm COD is quite shallow (less than 1 metre). In the derivation of bed depth, it was assumed

that the reactivity of the condensibles is unaffected by the extent of conversion.

6.1.1.3 Energy Requirements

One further important item for design purposes is the thermal requirement of the system. For this reaction, energy is needed to reform the reactants and in certain instances to bring the gas to reaction temperature. The requisite energy for gas heating is .0015 $MJ/Nm^3/°C$ (.038 BTU/scf/°C) which, for a typical low Joule value gas of $6MJ/Nm^3$, is a small fraction of the total gas energy (1% for a maximum temperature increase of 50°C).

From the condensate evaluation by Duncan (1981), it is assumed that the empirical analyses is $CH_{1.06}O_{0.21}$ with a higher heating value of 31.4 MJ/kg (13,500 BTU/lb). The heat of the reforming reaction is thus 6.72 MJ/Kg (2,890 BTU/lb.) condensate converted. If it is assumed that the gas contains 2% tar, by weight, then the heat required to reform all of the tar is .15 MJ/Nm^3 (3.8 BTU/scf) or about 2.5% of the heating value of the gas. This heat is, of course, recovered on combustion. In this instance, the gas temperature will drop about 100°C across the reformer.

From the above discussion, it is obvious that the operational requirements for the reforming process are all

within the acceptable limits for commercial operation.

6.1.2 Reforming in Conjunction with Power Generation

In this example, a downdraft gasifier is combined with a diesel engine to generate power. The diesel engine requires a cool clean gas which is usually accomplished by water scrubbing the raw gas. In the case of a downdraft gasifier, the temperature of the low BTU gas is typically in the range 400 - 600°C.

The key question regarding the use of reforming in conjunction with a downdraft gasifier is in reference to the particulate loading of the gas stream. While differing claims have been made regarding downdraft gasifiers, the consensus tends to indicate that the gas does contain sufficient particulate to create problems in a packed catalyst bed. There are three potential remedies to this: electrostatic precipitation, dual catalyst beds with backflush or catalyst fluidization in conjunction with conventional wet scrubbing. The choice of a cleaning system is very much a function of particulate loading and gas flow i.e. for small gasifiers and relatively clean gas, dual catalyst beds would be the preferred choice while for large atmospheric pressure units, electrostatic precipitation could be utilized. On the other hand, pressurized systems could effectively absorb the pressure

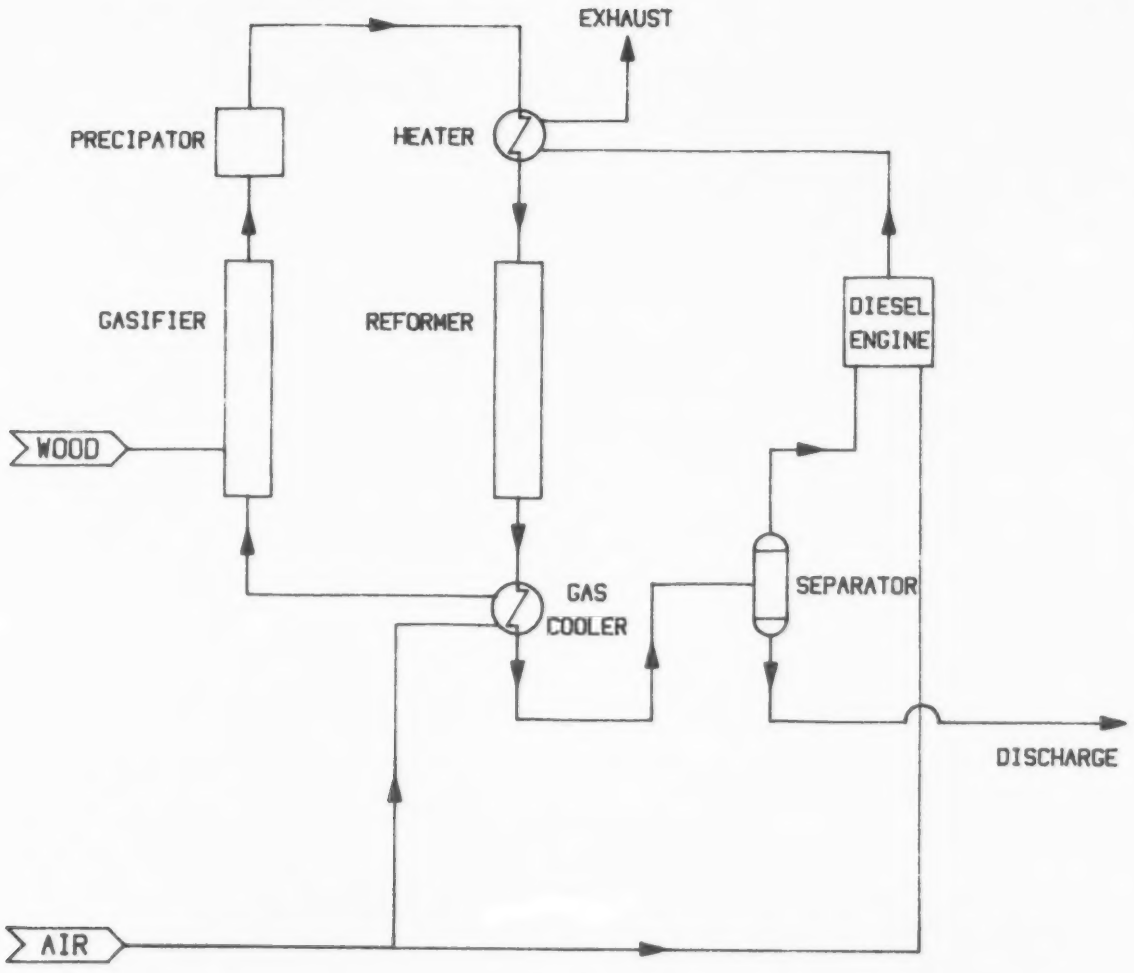
drop of a fuidized bed reformer.

Figure 14 illustrates the principles involved in a system incorporating an electrostatic precipitator. Gas from the gasifier is cleaned in an electrostatic precipitator, then preheated, if required, to 550 - 600°C by a combination of air injection and an interchanger, before it is piped to the packed catalyst bed. After the tars are dissociated, the gas is cooled through the interchanger. Since the tars have been removed, additional heat can be recovered to preheat the air for the gasifier prior to cooling for delivery to the engine. All piping must be effectively insulated to prevent heat loss and tar deposition prior to reforming. It is important to note that any heat added to the system can be recovered for drying or preheating the gasifier air. The thermal efficiency should remain the same or even higher since the sensible heat from the gas can be recovered to a much lower temperature and more than 99% of the heat in the tar is recovered for use in the engine.

6.1.3 Reforming for Pipeline Use

Pipeline transmission of low or medium BTU wood gas has not yet been commercialized but it is an effective means of distributing the gas from a large central gasifier with minimum loss of efficiency. It is not expected that the distances would be long e.g. 1 to 40 km. Typical

FIGURE 14. POWER GENERATION GASIFIER WITH A REFORMER



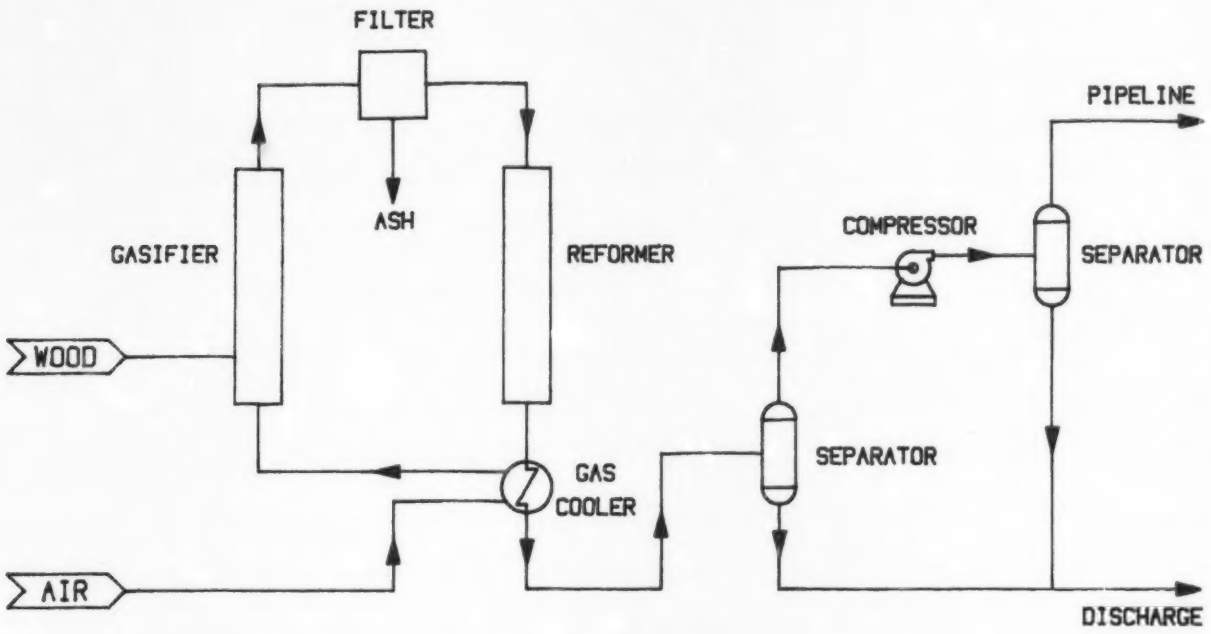
a) Fixed bed reformer with hot gas cleaning

applications might include a central municipal refuse plant with a gasifier for distributing low BTU gas to a number of different users or, a large industrial plant with distributed energy units.

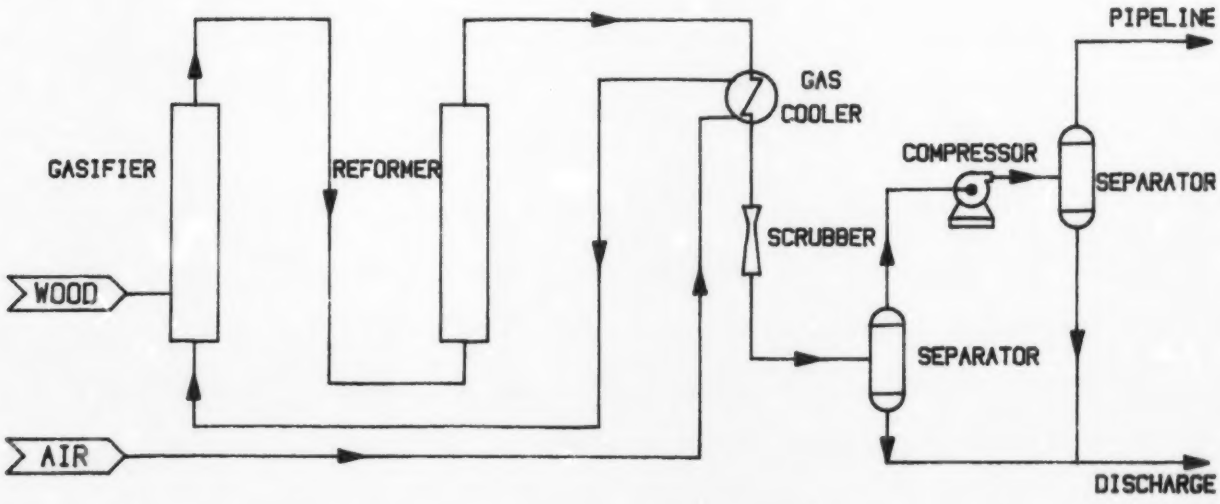
To be effective, the gas must be clean, dry and pressurized. For this application, it will be assumed that a fluidized bed gasifier is used. In this instance, since the gas from a fluidization unit is normally in excess of 700°C, there are at least two process routes that can be selected; hot gas cleaning, followed by a fixed bed reformer, gas cooling, compression, if necessary, and dehydration or, a fluidized bed reformer, with gas cooling, scrubbing, compression and dehydration. Block diagrams of each are illustrated in figure 15. The capital and operating costs are probably not too different for either case and a site specific economic analysis would be required before a definitive selection could be made. The efficiency of the process is unchanged by reforming and may, in fact, benefit because of the availability of more sensible heat and the recovery of the tar heating values.

The above descriptions confirm that reforming can be adapted to a broad range of gasifiers with different end uses. Operating efficiencies are relatively unaffected and all of the required process equipment is well proven in other uses. It is also obvious that the process must be tailored to the

FIGURE 15. A PIPELINE GASIFIER WITH A REFORMER



a) Fixed bed reformer with hot gas cleaning



b) Fluidized bed gasifier with scrubbing

specific gasifier and the end use, in order to maximise the benefits obtained.

6.2 Comparison With Other Processes

In the past, gasifier applications involving the quenching of gas have been sufficiently small that the effluent has not been treated before discharge. This will not be permitted on a larger scale since the effluent has a high BOD_5 and is potentially mutagenic. As a result, conventional waste-water treatment technologies are not currently applicable but there are a number of systems under development. Most of these are aimed at treatment of the effluent with advanced wastewater technologies such as activated carbon, anaerobic digestion, extraction and wet oxidation. Other potential routes include drying to reduce condensate volume in conjunction with combustion of the condensate.

All of these processes are in an early stage of development. Beck (1980) concluded that activated carbon alone was not effective, while solvent extraction, Bell (1980), also shows little promise. Conventional biological treatment processes have difficulty in achieving satisfactory COD reductions. The more recent approaches, involving film reactors, show more effectiveness but neither aerobic nor anaerobic treatment alone can achieve a satisfactory

reduction in COD. It is only when they are used in conjunction, Bell (1980), that high efficiencies can be achieved, 94 - 98%. This is still not high enough to achieve a satisfactory effluent for discharge. If it is assumed that the outlet COD must be 60 ppm maximum, then the required overall efficiency is 99.85%.

Since it appears that even more sophisticated water treatment technology will be required, it is concluded that reforming with its demonstrated high efficiency, simple catalysts and equipment, and ease of operation will be very competitive with other technologies. It is, however, recommended that a more detailed review of costs be evaluated when sufficient data is available from the investigations which are currently underway.

7.0 CONCLUSIONS

The following are the conclusions from the study:

- A review of the literature revealed a wide diversity of materials occurring in biomass gasifier condensates.
- From thermodynamic derivations, reforming at temperatures above 450°C can theoretically eliminate pollution resulting from the cooling and condensation of the gas from biomass gasifiers.
- Experimental tests confirmed that reforming kinetics are sufficiently rapid to achieve low contamination levels.
- The reforming reaction is mass transfer limited under the conditions used in experimental program.
- Alumina, limestone and nickel are all equally effective under the experimental conditions.
- Reforming of the gas does not affect the more permanent hydrocarbons e.g. methane, ethylene etc. and hence has minimal effect on the heating value of the gas.
- The conditions required to attain effective treatment, temperatures in excess of 450°C with equivalent reactor lengths of 1 m or less are commercially viable.
- Reforming is as effective if not more so than other technologies.

- With the limited information that is available, the costs associated with reforming are competitive with alternates.

8.0 RECOMMENDATIONS

Since reforming appears to be an effective competitive technology for elimination of pollution from gasifier condensates, it is recommended that:

- Long term studies be conducted to evaluate the potential effects of catalyst poisoning, carbon deposition and particulate fouling.
- As further information becomes available, a preliminary economic evaluation of condensate treatment technologies be carried out.
- Efforts be made to commercialize the technology if further evaluations continue to be promising.

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A.0 CALCULATION OF EQUILIBRIUM CONSTANT

A.1 Theoretical Discussion

One of the principal reactions under investigation in this study is the reaction between steam and the organic vapours present in the raw gas from biomass gasifiers, i.e.

$$C_aH_bO_c + (a-c)H_2O \longrightarrow aCO + (a-c+b/2)H_2$$

The equilibrium constant for the reaction is given by

$$Ka = \frac{(a_{CO})^a \cdot (a_{H_2})^{(a-c+b/2)}}{a_{CaHbOc} \cdot (a_{H_2O})^{(a-c)}} \qquad \ldots\ldots(a.1)$$

where a_i, representing the activity of component i, is defined by

$$a_i = \frac{\bar{f}_i}{f_i^o} \qquad \ldots\ldots(a.2)$$

where $\bar{f}_i^o$ is the fugacity at the standard reference state and f_i is the fugacity of component i in a mixture. By choosing unit fugacity as the reference state, then

$$a_i = \bar{f}_i \qquad \ldots\ldots(a.3)$$

However, the fugacity of a real gas is given by

$$\bar{f}_i = Y_i \, P \, \phi_i \qquad \text{.....(a.4)}$$

where Y_i is the mole fraction of component i in the gas mixture, P is the total gas pressure and ϕ is the fugacity coefficient. Substitution in (a.3) yields

$$a_i = Y_i \, P \, \phi_i \qquad \text{.....(a.5)}$$

and substitution of (a.5) in (a.1) gives

$$Ka = \frac{(Y_{CO}.P)^a.(Y_{H_2}.P)^{a-c+b/2}}{(Y_{CaHbOc}.P).(Y_{H_2O}.P)^{a-c}} \cdot \frac{\phi_{CO}^a \cdot \phi_{H_2}^{a-c+b/2}}{\phi_{CaHbOc} \cdot \phi_{H_2O}^{a-c}} \qquad \text{.....(a.6)}$$

which can be simplified through standard nomenclature to

$$Ka = Kp \cdot K\phi \qquad \text{.....(a.7)}$$

For many gases and vapours, the fugacity coefficient approximates 1 at low pressure and high temperature, hence

$$Ka = Kp = \frac{Y_{CO}^a \cdot Y_{H_2}^{a-c+b/2}}{Y_{CaHbOc} \cdot Y_{H_2O}^{a-c}} \cdot P^{a-1+b/2} \qquad \text{.....(a.8)}$$

Equation (a.8) provides a means of calculating the equilibrium concentration of the organic vapour when Ka is

known.

The van't Hoff isotherm furnishes a route whereby the equil rium coefficient can be calculated from tabulated thermodynamic data as follows:

$$\Delta F_i^o = -RT \ln Ka \qquad \text{.....(a.9)}$$

Where R is the gas constant, T the absolute temperature °K and F_i^o the Gibbs free energy of component i at the standard reference state. Δ indicates the incremental change in a property for any given reaction.

Many of the thermodynamic data involving F_i^o are given in the form $(F^o - H^o)/T$ where H^o = enthalpy at the standard reference state. Rearrangement of this term yields

$$\frac{\Delta(F^o - H^o_{298})}{T} = \frac{\Delta F^o}{T} - \frac{\Delta H^o_{298}}{T} \qquad \text{.....(a.10)}$$

Where H^o_{298} is the enthalpy in the standard reference state at 298°K. Rearrangement gives

$$\frac{\Delta F^o}{T} = \frac{\Delta H^o_{298}}{T} - \frac{\Delta(F^o - H^o_{298})}{T} \qquad \text{.....(a.11)}$$

Modification of (a.9) yields

$$\frac{\Delta F^\circ}{T} = -R \ln Ka \qquad \text{.....(a.12)}$$

Substitution in equation (a.11) gives

$$\ln Ka = R\left\{\frac{\Delta H^\circ_{298}}{T} - \frac{\Delta(F^\circ - H^\circ_{298})}{T}\right\} \qquad \text{.....(a.13)}$$

The values of H°_{298} and $(F^\circ - H^\circ_{298})/T$ are readily available in standard texts for many organic compounds, thus enabling Ka to be calculated.

A.2 Calculation of Equilibrium Constants

Equation (a.13) provides a ready means of calculating the steam reforming equilibrium constants for the materials found in gasifier condensates. Unfortunately, it was not possible to obtain the necessary thermodynamic data for each of the chemicals identified in Table 1. However, one source, Stull et. al. (1969), did contain the properties, H°_{298} and $(F^\circ - H^\circ_{298})/T$, for the majority of the members of each homologous series identified in Table 1. For consistency and simplicity, it was decided that this compilation would be used as the sole data source for the evaluation of the equilibrium constants and that any component not documented would not be evaluated. Because the behaviour pattern is apparent from the lower members of

each homologous series, these omissions do not materially affect the conclusions of the study.

Since all of the organic components considered in the evaluation were present in low concentrations (less than 2%), it was therefore assumed that, at the temperatures selected, these compounds would behave as ideal gases and that

$$Kp = Ka$$

Thus

$$\ln Kp = -R \left\{ \frac{\Delta H^{o}_{298}}{T} - \frac{\Delta (F^{o} - H^{o}_{298})}{T} \right\} \quad ....(a.14)$$

A short computer program, based on equation (a.14), was developed to calculate the equilibrium constant Kp over the temperature range 300 to 1000°K. Typical values for the constants are presented in Table A-1 and Figure 1.

A.3 Calculation of Equilibrium Concentrations

As a further development of equation (a.13), the equilibrium concentrations of certain key condensate components were calculated for particular prescribed conditions. To simulate the ultimate effects of reforming on the

TABLE A-1

The Effect of Temperature on Reforming Equilibrium Constants

Chemical Component	Units	Temperature °K				
		300	500	700	900	1000
Methane	atm^{-1}	2.1 × 10^{-23}	8.6 × 10^{-11}	2.6 × 10^{-4}	1.7	26.1
Ethane	atm^{-2}	4.1 × 10^{-38}	1.7 × 10^{-17}	1.4 × 10^{-5}	2.2 × 10^{0}	3.5 × 10^{3}
Propane	atm^{-3}	2.6 × 10^{-52}	4.9 × 10^{-23}	2.0 × 10^{-7}	1.2 × 10^{0}	1.7 × 10^{3}
n-Butane	atm^{-4}	4.9 × 10^{-67}	6.6 × 10^{-29}	1.5	5.1 × 10^{0}	5.8 × 10^{3}
iso-Butane	atm^{-4}	1.1 × 10^{-67}	5.7 × 10^{-29}	2.3	1.0 × 10^{1}	1.3 × 10^{4}
n-Pentane	atm^{-5}	2.5 × 10^{-81}	1.7 × 10^{-34}	21	3.0 × 10^{1}	3.0 × 10^{4}
Ethylene	atm^{-1}	1.5 × 10^{-20}	1.4 × 10^{-9}	69	4.5 × 10^{2}	1.0 × 10^{4}
propene	atm^{-2}	2.4 × 10^{-37}	8.1 × 10^{-17}	49	2.4 × 10^{2}	5.5 × 10^{4}
Butene - 1	atm^{-3}	1.1 × 10^{-51}	2.0 × 10^{-22}	6.4 × 10^{2}	1.4 × 10^{3}	2.9 × 10^{5}
Cis-Butene - 2	atm^{-3}	1.7 × 10^{-52}	7.6 × 10^{-23}	4.4 × 10^{2}	1.4 × 10^{3}	3.2 × 10^{5}
Trans-Butene - 2	atm^{-3}	4.0 × 10^{-51}	4.2 × 10^{-22}	2.9 × 10^{2}	9.8 × 10^{2}	2.3 × 10^{5}
Acetylene	atm^{-1}	4.9 × 10^{4}	2.3 × 10^{7}	4.4 × 10^{8}	2.7 × 10^{9}	5.1 × 10^{9}
Benzene	atm^{-3}	2.9 × 10^{-33}	2.2 × 10^{-13}	0.21	5.4 × 10^{1}	1.3 × 10^{4}
Toluene	atm^{-4}	2.0 × 10^{-50}	6.1 × 20^{-20}	7.1 × 10^{-2}	1.3 × 10^{1}	3.2 × 10^{3}
m-Xylene	atm^{-5}	8.5 × 10^{-107}	9.5 × 10^{-34}	0.15	2.1 × 10^{1}	5.3 × 10^{3}
p-Xylene	atm^{-5}	2.1 × 10^{-106}	2.2 × 10^{-33}	0.32	4.7 × 10^{1}	1.2 × 10^{4}
Cumene	atm^{-5}	1.8 × 10^{-111}	3.4 × 10^{-36}	15	9.2 × 10^{2}	1.3 × 10^{5}
Naphthalene	atm^{-5}	2.6 × 10^{-120}	3.3 × 10^{-38}	3.9 × 10^{-2}	8.4 × 10^{0}	1.2 × 10^{3}
1-Methylnaphthalene	atm^{-6}	3.6 × 10^{-137}	2.0 × 10^{-43}	2.9 × 10^{-2}	4.6 × 10^{0}	6.6 × 10^{2}
1,2 Dime naphthalene	atm^{-7}	3.0 × 10^{-153}	7.0 × 10^{-49}	.12	1.3 × 10^{1}	1.9 × 10^{3}
Azulene	atm^{-5}	5.7 × 10^{-98}	7.8 × 10^{-33}	1.4 × 10^{0}	2.2 × 10^{2}	5.7 × 10^{3}
Furan	atm^{-2}	3.5 × 10^{-34}	1.5 × 10^{-13}	1.6 × 10^{0}	7.7 × 10^{1}	7.7 × 10^{3}
Methanol	atm^{-1}	4.8 × 10^{-5}	1.7 × 10^{2}	1.8 × 10^{3}	9.4 × 10^{3}	3.4 × 10^{4}
Ethanol	atm^{-2}	6.9 × 10^{-22}	1.1 × 10^{-3}	1.3 × 10^{3}	5.1 × 10^{3}	2.1 × 10^{4}
Formic Acid	atm^{0}	4.3 × 10^{2}	3.5 × 10^{4}	2.4 × 10^{5}	7.0 × 10^{5}	1.0 × 10^{6}
Acetic Acid	atm^{-1}	2.2 × 10^{-19}	2.9 × 10^{-3}	1.3 × 10^{4}	6.9 × 10^{4}	1.4 × 10^{5}
Phenol	atm^{-3}	9.4 × 10^{-62}	2.4 × 10^{-16}	2.2 × 10^{4}	3.7 × 10^{5}	3.3 × 10^{5}
p-Cresol	atm^{-4}	2.6 × 10^{-78}	2.4 × 10^{-21}	2.4 × 10^{4}	2.9 × 10^{5}	2.6 × 10^{5}

gasification process, conditions, typical of those in which cooling and condensation of the gas stream might be encountered, were chosen i.e. for applications involving engine usage and synthesis gas production. In order to incorporate the extremes, two operating pressures were considered, 1 atmosphere and 20 atmospheres absolute. At the lower pressure two feedstocks were reviewed, wet and dry biomass, using air as the gasifying medium while the high pressure application was assumed to utilize dry biomass and oxygen. The raw gas concentrations for each simulation are described in Table A-2.

For the purpose of the estimate, it was further assumed that the behaviour of each component was independent of the others. This was essentially correct because of the low initial concentration of each component and the comparative excess of water, carbon monoxide and hydrogen.

The results of these analyses are presented in Tables A-3, A-4 and A-5 and Figures 2 and 3.

TABLE A-2

Assumptions for Evaluation of Equilibrium Concentrations

Component	Low Pressure		High Pressure
	Wet	Dry	Dry
	Concentration (mol %)	Concentration (mol %)	Concentration (mol %)
H_2O	25	8	17
H_2	10	15	18
CO	15	20	37
CO_2	11	11	15
CH_4	2	4	13
N_2 etc.	37	42	--

TABLE A-3

Equilibrium Concentration at Atmospheric Pressure (dry wood)

Chemical Component	Concentration (Mole Fraction)		
	700°K	900°K	1000°K
Methane	-	6.6×10^{-3}	3.2×10^{-4}
Ethane	3.3×10^{-2}	2.1×10^{-8}	1.4×10^{-10}
Propane	1.4×10^{-4}	2.0×10^{-13}	1.6×10^{-16}
n-Butane	9.7×10^{-7}	3.0×10^{-18}	2.6×10^{-22}
iso-Butane	6.5×10^{-7}	1.5×10^{-18}	1.2×10^{-22}
n-Pentane	4.1×10^{-9}	2.8×10^{-23}	2.8×10^{-28}
Ethylene	4.4×10^{-5}	7.1×10^{-9}	3.1×10^{-10}
Propene	3.7×10^{-6}	7.5×10^{-13}	3.2×10^{-15}
Butene-1	1.6×10^{-8}	7.0×10^{-18}	3.5×10^{-21}
Cis-Butene-2	2.3×10^{-8}	7.1×10^{-18}	3.1×10^{-21}
Trans-Butene-2	3.5×10^{-8}	1.0×10^{-17}	4.4×10^{-21}
Acetylene	4.8×10^{-11}	7.9×10^{-12}	4.1×10^{-12}
Benzene	4.5×10^{-5}	1.7×10^{-17}	7.3×10^{-22}
Toluene	7.4×10^{-6}	3.9×10^{-21}	1.6×10^{-26}
m-Xylene	2.0×10^{-7}	1.4×10^{-25}	5.6×10^{-32}
p-Xylene	9.1×10^{-8}	6.3×10^{-26}	2.5×10^{-32}
Cumene	1.1×10^{-10}	1.8×10^{-30}	1.3×10^{-38}
Naphthalene	7.1×10^{-7}	3.3×10^{-27}	2.3×10^{-34}
1-Me naphthalene	5.3×10^{-8}	3.4×10^{-31}	2.4×10^{-39}
1,2-Dime naphthalene	7.2×10^{-10}	6.6×10^{-36}	4.6×10^{-45}
Azulene	2.0×10^{-16}	1.3×10^{-34}	4.9×10^{-41}
Furan	1.5×10^{-13}	3.1×10^{-19}	3.1×10^{-21}
Methanol	2.5×10^{-8}	5.3×10^{-10}	1.3×10^{-10}
Ethanol	1.9×10^{-9}	4.9×10^{-14}	1.2×10^{-15}
Formic Acid	6.6×10^{-8}	2.3×10^{-8}	1.6×10^{-8}
Acetic Acid	7.0×10^{-8}	1.3×10^{-11}	6.6×10^{-13}
Phenol	2.3×10^{-10}	1.3×10^{-21}	1.5×10^{-25}
o-Cresol	1.2×10^{-11}	9.6×10^{-26}	1.1×10^{-30}

TABLE A-4

Equilibrium Concentration at Atmospheric Pressure (wet wood)

Chemical Component	Concentration (Mole Fraction)		
	700°K	900°K	1000°K
Methane	-	4.7×10^{-4}	2.3×10^{-5}
Ethane	2.5×10^{-4}	1.6×10^{-10}	1.0×10^{-12}
Propane	1.1×10^{-7}	1.6×10^{-16}	1.3×10^{-19}
n-Butane	8.4×10^{-11}	2.6×10^{-22}	2.2×10^{-26}
iso-Butane	5.6×10^{-11}	1.3×10^{-22}	1.0×10^{-28}
n-Pentane	3.8×10^{-14}	2.5×10^{-38}	2.6×10^{-33}
Ethylene	5.3×10^{-7}	8.0×10^{-11}	3.6×10^{-12}
Propene	4.4×10^{-9}	9.1×10^{-16}	3.9×10^{-18}
Butene-1	2.0×10^{-12}	9.1×10^{-22}	4.6×10^{-25}
Cis-Butene-2	3.0×10^{-12}	9.1×10^{-22}	4.0×10^{-25}
Trans-Butene-2	4.5×10^{-12}	1.3×10^{-21}	5.7×10^{-25}
Acetylene	8.1×10^{-13}	1.4×10^{-13}	7.1×10^{-14}
Benzene	2.2×10^{-10}	8.6×10^{-23}	3.6×10^{-27}
Toluene	3.9×10^{-12}	2.1×10^{-27}	8.7×10^{-33}
m-Xylene	1.2×10^{-14}	7.9×10^{-33}	3.2×10^{-39}
p-Xylene	5.2×10^{-15}	3.6×10^{-33}	1.4×10^{-39}
Cumene	6.8×10^{-19}	1.1×10^{-38}	7.8×10^{-47}
Naphthalene	1.6×10^{-15}	7.2×10^{-36}	5.1×10^{-43}
1-Me naphthalene	1.2×10^{-17}	8.0×10^{-41}	5.5×10^{-49}
1,2-Dime naphthalene	1.8×10^{-20}	1.6×10^{-46}	1.1×10^{-55}
Azulene	4.4×10^{-25}	2.7×10^{-43}	1.1×10^{-49}
Furan	2.0×10^{-16}	4.2×10^{-22}	4.2×10^{-24}
Methanol	8.4×10^{-9}	1.8×10^{-10}	4.4×10^{-11}
Ethanol	6.8×10^{-11}	1.8×10^{-15}	4.2×10^{-17}
Formic Acid	1.5×10^{-7}	5.3×10^{-8}	3.8×10^{-8}
Acetic Acid	1.7×10^{-8}	3.3×10^{-12}	1.7×10^{-13}
Phenol	5.3×10^{-15}	3.1×10^{-26}	3.5×10^{-30}
o-Cresol	2.9×10^{-17}	2.4×10^{-31}	2.7×10^{-36}

TABLE A-5

Equilibrium Concentration at 20 Atmospheres (dry wood)

Chemical Component	Concentration (mole fraction)		
	700°K	900°K	1000°K
Methane	-	-	.194
Ethane	-	6.3×10^{-13}	4.1×10^{-5}
Propane	-	3.1×10^{-5}	2.3×10^{-8}
n-Butane	-	2.3×10^{-7}	2.0×10^{-11}
iso-Butane	-	1.1×10^{-7}	8.8×10^{-12}
n-Pentane	-	1.1×10^{-9}	1.1×10^{-14}
Ethylene	(0.58)	8.9×10^{-5}	3.9×10^{-6}
Propene	-	4.7×10^{-6}	2.0×10^{-8}
Butene-1	-	2.2×10^{-8}	1.1×10^{-11}
Cis-Butene-2	-	2.2×10^{-8}	9.8×10^{-12}
Trans-Butene-2	-	3.2×10^{-8}	1.4×10^{-11}
Acetylene	2.5×10^{-8}	4.2×10^{-9}	2.2×10^{-9}
Benzene	-	9.9×10^{-7}	4.2×10^{-11}
Toluene	-	1.1×10^{-7}	4.7×10^{-13}
m-Xylene	-	2.0×10^{-9}	8.0×10^{-16}
p-Xylene	-	9.1×10^{-10}	3.6×10^{-16}
Cumene	-	1.3×10^{-11}	9.4×10^{-20}
Naphthalene	-	8.8×10^{-10}	6.1×10^{-17}
1-Me naphthalene	-	4.5×10^{-11}	3.2×10^{-19}
1,2-Dime naphthalene	-	4.4×10^{-13}	3.0×10^{-22}
Azulene	-	3.3×10^{-17}	1.3×10^{-23}
Furan	1.4×10^{-6}	3.0×10^{-12}	3.0×10^{-14}
Methanol	2.7×10^{-5}	5.7×10^{-7}	1.4×10^{-7}
Ethanol	1.0×10^{-3}	2.6×10^{-8}	6.4×10^{-10}
Formic Acid	5.2×10^{-6}	1.8×10^{-6}	1.3×10^{-6}
Acetic Acid	2.7×10^{-3}	5.2×10^{-7}	2.6×10^{-8}
Phenol	-	1.4×10^{-10}	1.5×10^{-14}
o-Cresol	-	4.9×10^{-12}	5.5×10^{-17}

POOR

QUALITY

ORIGINAL